Development of Ultrasonic Techniques for Characterization of Liquid Mixtures

William A. Cooke

The University of Western Ontario

Supervisor
Anand Prakash
The University of Western Ontario

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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ABSTRACT

To evaluate the suitability of ultrasonic techniques for on-line process monitoring applications, an ultrasonic probe was used to measure acoustic velocity, acoustic impedance, and isentropic compressibility of hydrocarbons (including n-, iso-, and cycloalkanes, toluene, mineral oil, and crude oil) and polar liquids (alcohols, water, salt water) over a temperature range of 25-60°C. Temperature, carbon chain length, molecular shape, and intermolecular forces had significant effects on ultrasonic parameters. Relationships between media characteristics and observed ultrasonic parameters were modeled using empirical-least squares equations. The same parameters were measured in binary mixtures of hydrocarbons in heptane, as well as polar liquids in ethanol. Experimental values were presented as a function of volume fraction and compared to ideal mixing conditions. Excess quantities were computed and shown in a similar manner. Ultrasonic techniques were demonstrated to be effective in estimating ethanol content in n-heptane (representing gasoline) and for detecting volatile losses for stored crude oil.

KEYWORDS:
Ultrasonic technology
Process monitoring
On-line applications
Acoustic velocity
Isentropic compressibility
Acoustic impedance
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Chapter 1: Introduction

Over the past decade many social and economic factors have inspired new chemical processes and innovations to existing ones, largely in an effort to reduce environmental impact. As companies strive to optimize these processes, process monitoring becomes integral to their success. This has resulted in a rapidly growing market for inexpensive and robust process monitoring technology capable of on-line operation.

One specific area of interest for online monitoring is the characterization of liquid mixtures. There are several conventional techniques for analyzing liquid mixtures, however limitations of these methods have been identified in literature and are discussed in this report.

Applications of ultrasonic technology for spectroscopic purposes are becoming more commonplace. This is in part due to their versatile nature, as their function does not require an optically active or conducting medium. Nor does it require sample preparation or human operation in most cases. Other favourable qualities of ultrasonic technology include:

- Fast response time, near instantaneous readings are favourable for on-line applications
- Non-destructive sampling techniques
- Hardware is compact
- Associated costs are trending downward as technology becomes more widespread

This project contains a comprehensive review of literature pertaining to ultrasonic technology, including an overview of existing and emerging ultrasonic applications, and descriptions of existing alternatives most commonly used in industry.

Following the review of literature, a comprehensive study of ultrasonic behaviour in different liquids is performed. These experiments are split into two chapters based on liquid class; the first involving non-polar hydrocarbons and their mixtures, the second focusing on polar liquids and
their mixtures. Trends in the behaviour of ultrasonic parameters with respect to properties of the liquids under investigation are identified and accounted for using molecular and fluid dynamics. Trends are then evaluated for viability of being implemented into ultrasonic liquid characterization technology.

1.1 Objectives

This project aims to demonstrate that variability in measurable ultrasonic quantities across different classes of liquids are significant, and can be used to characterize an unknown homogeneous liquid. In addition to demonstrating viability, designs for technology employing ultrasonic techniques for specific applications pertaining to liquid characterization will be proposed.
Chapter 2: Literature Review

2.1 Introduction

In processing and upgrading industries the composition of liquids are constantly undergoing changes throughout the plant. Such industries include crude oil processing, edible oil processing, bio-refining and many others. In each of these industries a complex network of different units is used to convert raw materials into final products, making it difficult to identify the root of a problem if a product fails to meet specifications or is otherwise flawed. To mitigate this type of risk, it is crucial that liquid compositions of both final and intermediate products are monitored in any given process. This is especially true of highly regulated and sensitive processes that produce a wide range of products. A prime example of this type of process is downstream crude oil refining.

In its raw state, crude oil can have salinity levels as high as 20wt%, depending on the source (Mohamed et al., 2003). Salt content this high can cause problems with refinery operations and equipment including corrosion, catalyst deactivation, and fouling. To prevent these sorts of issues salt is removed from the crude oil before it is further processed. This operation is performed in an aptly named component called a Crude Oil Desalter (Fortuny, et al., 2007). The primary mechanism employed by a desalter is liquid-liquid extraction, using water as a solvent to extract mineral salts from the oil. The agitation and immiscible nature of the oil-water mixture causes an emulsion layer to form between the two liquid layers upon settling. The emulsion layer consists of many small bubbles of one liquid scattered throughout another; the dispersed phase and continuous phase, respectively. Creating an emulsion is crucial for providing sufficient surface area for the diffusion of salt from the organic to the aqueous phase. However, these emulsions often stabilize and as such become difficult to separate. The size of the emulsion layer thus grows over time, increasing the risk of emulsion exiting through the oil or wastewater streams. Allowing the
emulsion layer to enter refinery operations has the potential to cause a host of uniquely challenging problems in downstream units (Kocherginsky et al., 2003). By monitoring the liquid compositions of the desalter’s product streams, these types of issues can be avoided.

A notable issue that is getting more attention as-of-late is the loss of volatile ends from stored crude oil, via evaporation. Evaporation is a major source of loss in the crude oil industry, and with crude oil stores at an all-time high, reaching 1.227 Billion Barrels as of June 6th 2016 (EIA, 2016), the problem is of growing concern. Light end losses are costly from both environmental and financial viewpoints, as light end hydrocarbons are especially valuable and contribute to pollution when allowed to enter the atmosphere. While liquid composition monitoring technique is not useful on its own for preventing evaporation, it can be used to estimate the rate and magnitude of losses using the composition of the remaining liquid mixture.

Another recent trend affecting the oil and gas sector is the increased importance of environmental stewardship. This shift in attitude has put pressure on petroleum companies to reduce their environmental impact by incorporating renewable resources into existing products. Perhaps the most widespread use of renewable resources in the oil and gas sector is the use of ethanol in gasoline. Approximately 97% of gasoline in the United States contains some ethanol, the most common blend being 10% ethanol by volume (U.S. Department of Energy, 2016). When blending ethanol with gasoline it is important that the ethanol be fuel-grade, or anhydrous. This is because water-ethanol mixtures, even with only minimal amounts of water, are insoluble in gasoline. This results in a two-phase liquid mixture which could be harmful to a vehicle’s engine. It is therefore imperative that gasoline companies ensure ethanol is anhydrous before blending. Some common techniques for measuring water content in gasoline include density analysis, infrared and near-infrared spectral methods, and Karl Fischer titration.
In some countries suppliers of gasoline are legally obligated to blend their products with gasoline. Canada for example, as of December 2010 requires that gasoline contain at least 5% ethanol by volume and that suppliers submit annual reports including records of measurement of ethanol content (Government of Canada, 2013). Several current and emerging spectroscopic techniques for determining ethanol content exist, including gas chromatography, infrared spectroscopy, and high-performance liquid chromatography. However, most techniques require human operation and analysis and few are suitable for making real-time measurements. When using liquid monitoring to monitor time sensitive events such as detecting losses, and drastic changes in feedstock or product stream concentrations it is important that information is relayed to the operator or control system quickly. Reduced response times allow for problems to be resolved faster and thus minimize their adverse effects. A continuous monitoring technique would also serve to reduce response time, as any fluctuations in concentration would be detected immediately. Whereas intermittent sampling techniques could allow an event to go unnoticed for a length of time as long as the sampling period. With increased sampling it becomes more important to employ non-invasive and non-destructive sampling techniques in order to minimize the impact sampling has on the existing process and to limit waste. Therefore, the ideal monitoring technique is continuous, can display data in real time for online applications, is non-invasive and employs non-destructive sampling techniques. The following sections will review literature pertaining to ultrasonic technology and liquid characterization. Including current technology for liquid analysis, an overview of ultrasonic principles, and a review of available and emerging ultrasonic technology relevant to the project.
2.2 Overview of existing liquid characterization technologies

2.2.1 Gas chromatography mass spectrometry

The most common technique used for determining the composition of a liquid mixture employs both gas chromatography and mass spectrometry, and is often referred to as GC-MS. Gas chromatography is a separation technique that separated components of a mixture based on their volatility and is used to determine the concentration of species in a given mixture. While mass spectrometry ionizes molecules and identifies them based on their mass to charge ratio. The combined process, GC-MS, allows users to generate a reliable assay of a given liquid mixture (Chauhan et al., 2014). GC-MS is a proven technology and is used for determining the composition of unknown liquids in a wide range of disciplines. Some of which include environmental analysis, pesticide analysis for food safety, pharmaceutical and drug analysis, forensic and clinical toxicology, crime scene analysis, and of course the petrochemical industry (Sahil et al., 2011).

Initially the sample under investigation is dissolved in an organic solvent, the mixture is then injected into gas chromatograph where it is instantly vapourized by way of heat. A pressurized inert gas (the mobile phase) is then mixed with the vapour, forcing the resulting mixture through a thin tube, known as a capillary column. The column is packed with a high boiling liquid (the stationary phase), which interacts with the different components of the mixture via absorption and desorption. This slows the mixture down and facilitates separation based on volatility of the individual components. The time it takes for each component to travel through the entire capillary is known as the retention time, which is the characteristic used to distinguish between components.

A printout will display several peaks, each one corresponding to a different component in the mixture. The area under each peak is proportional to the fraction of the mixture that its corresponding component accounts for. After separation by GC each component is fed into the
mass spectrometer. There, molecules are bombarded with electrons causing them to fragment into unique cations. The resulting cations are filtered using a magnetic field, after which they are separated by their mass to charge ratio. From this a mass spectrum is created, which is essentially a bar graph with relative abundance on the vertical axis and mass to charge ratio on the horizontal axis. Molecules have unique mass spectra, and as such the resulting spectrum for each unknown compound can be used to identify it (Hites, 1997).

GC-MS is so widely used because of its adaptability, accuracy, column efficiency, and relatively fast analysis speed. However, GC-MS does not satisfy the criteria listed earlier for the ideal monitoring system. For example, gas chromatographs operate at a maximum temperature of ~325°C which is not sufficiently high to vaporize some of the heavier components found in crude oil, such as asphaltenes (Zeng et al., 2012). Subramanian et al. (1996) demonstrated that heavier ends could be analyzed using high temperature GC (HTGC). However, the high temperatures associated with HTGC are not suitable for lighter ends and as such samples must be separated beforehand. Another drawback to HTGC is that the components of the capillary and stationary phase need to be much more specialized and are thus more expensive. Both are constantly exposed to temperatures >400°C and the prolonged exposure to these temperatures would require frequent service and replacement (Zenget al., 2012).

Another limitation of GC-MS is that it is not suitable for continuous sampling or on-line use. Gas chromatography separates components based on how long it takes them to pass through capillary, and requires a finite amount of each component to be added. Components pass through the capillary sequentially creating peaks for each specie, however if there is a constant feed of liquid mixture no component will ever completely pass through the GC and therefore no peaks will be observed. Additionally, mixtures will be fed into the mass spectrometer instead of pure liquids so
the spectra will not match any found in the database. Wortberg et al. (2006) reported using GC-MS for online monitoring of industrial wastewater for 140 different contaminants. However, the cycle time of each test was 40 minutes which in a large industrial operation, could result in a great deal of loss before a problem is detected. In an attempt to reduce the cycle time two instruments were used, so the effective sampling period was 20 minutes. By further increasing the number of GC-MS systems the sampling period could theoretically be reduced to a reasonable amount of time, however this would not be very cost effective.

In applications like crude oil refining there are countless different components found in any single mixture, and the composition of said mixture changes constantly. Some of the strengths of GC-MS are its precision and sensitivity, but in crude oil applications these characteristics make it less suited for some applications. Two examples are monitoring losses or detecting drastic changes in overall composition. These applications do not need detailed assays of samples, they only need to be able to detect major changes; so performing GC-MS analysis on every sample would be a massive waste of computing power. Especially considering the number of mass spectra that would need to be indexed. A more simplistic monitoring technique should be employed and used to determine when further analysis via GC-MS is necessary.

2.2.2 High-performance liquid chromatography

High-performance liquid chromatography (HPLC), like GC, is a highly precise separation technique that is widely used in industry and academia. However, HPLC is not as commonly used in the petrochemical industry. Instead its use had become widespread in the food processing, polymer, and pharmaceutical industry. The reason for this being it separates components in the liquid phase and is thus appropriate for temperature sensitive and high-boiling samples, such as large polymers. After separating a mixture into its components, HPLC can be coupled with
spectroscopy to yield similar results as GC-MS. Usually UV-Vis or MS, depending on the application. HPLC equipment is highly accurate, however it is also extremely costly and for the same reasons as GC-MS, is not appropriate for on-line applications (Reuhs & Rounds, 2010; Svec, 2004).

2.2.3 Optical techniques

There exist many spectroscopic techniques that employ light of various wavelengths as a tool for characterizing liquids and/or suspensions. Two of these are laser diffraction (LD) and ultraviolet-visible spectrophotometry (UV-Vis). Laser diffraction is typically used for particle sizing within a suspension, emulsion, or powder (Eshel et al., 2004), while UV-Vis is more commonly used for determining concentration of a solution. However, UV-Vis is capable of measuring absorbance of gases and some solids (Förster, 2004).

![Figure 1: Idealized diffraction of light off of a spherical particle (HORIBA, 2016)](image)

The principle of particle sizing by laser diffraction is based on the principle that when a wavelength of amplified light comes into contact with a particle (or bubble) it will scatter the wave into many smaller waves. This is called diffraction, or scattering. The angle, and intensity profile of the resulting scattered waves are determined by the size of the particle. At the smaller end of the spectrum diffraction is isotropic, meaning the intensity of diffracted waves are equal in all
directioning (rayleigh scattering). As particle size increases diffraction begins to favour forward diffraction in the low angle direction. So based on the resulting reflected light pattern, one can draw conclusions about the size distribution of the particles under observation (Jawad et al., 2004). HORIBA Scientific (2016) states that their LA-960 particle size analyzer can measure particles in the range of 10nm to 5mm.

A UV-Vis spectrophotometer measures the concentration of a mixture based on the absorbance of a certain wavelength of visible, or ultraviolet light, through a given liquid. Light is emitted from the appropriate source lamp (there are two separate lamps for UV and visible light), and then passed through a slit to ensure all photons are travelling along parallel pathways. The light then strikes a prism (or grating) where it is split into its respective wavelengths. A second slit allows only a narrow range of light to pass through, which then passes through the sample and is subsequently picked up by the detector (Perkampus, 1992).

![Simplified schematic of UV-Vis spectrophotometer](image)

**Figure 2: Simplified schematic of UV-Vis spectrophotometer (Jensen, 2015)**

The detector will report a figure called transmittance, which is the ratio of the intensity of light after passing through the sample (P) and the intensity of the incident beam (P₀). The concentration of a given sample is related to transmittance via the Beer-Lambert law.

\[
A = -\log \left[ \frac{P}{P_0} \right] = \varepsilon [x] d
\]

\(1\)
Where \( A \) is absorbance, \( \varepsilon \) is the molar extinction coefficient, \([x]\) is the molar concentration, and \( d\) is the path length.

Concentration of a known constituent can therefore be determined if the molar extinction coefficient is available. Alternatively, it can be determined experimentally using solutions of known concentration, effectively creating a calibration curve for interpolation (Förster, 2004).

Unfortunately, optical based techniques, such as LD and UV-Vis are often not practical in petrochemical applications. This is because in general, liquids are opaque and absorb nearly all wavelengths of light. Therefore, absorption would be nearly 100% making signal detection almost impossible.

### 2.2.4 Conductivity

Currently the most commonly used technique for monitoring salinity or total dissolved solids of a given aqueous solution is via conductivity. Instrumentation measures the electric resistance in the water and from this determines the concentration of free floating ions such as Na\(^+\), Cl\(^-\) or K\(^+\). The drawback for this technique is that it does not work in non-conducting systems, such as organic liquids, making this unsuitable for use in many industries including most petrochemical and edible oil applications (Rhoades et al., 1976).

### 2.3 Overview of ultrasonic terms and principles

#### 2.3.1 General definition of ultrasound

Ultrasound refers to sound waves with frequencies that exceed the normal human audible limit of 20 kHz. In most fluids ultrasound presents a longitudinal waves, propagating via alternating compression and rarefaction of the media (Laugier & Haïat, 2011).
These zones are the result of cyclic perturbations that cause particles in the fluid to be displaced from their resting position. This creates the initial compression zone and causes collisions with adjacent particles inducing similar displacement. Due to the elastic nature of fluids, particles return to their initial equilibrium position, resulting in a rarified zone (Martin et al., 2015). This chain reaction continues, transmitting reactions step by step through the media. Since displacement caused by the passage of the acoustic waves is infinitesimally small, it can be safely assumed to be harmonic in nature. Meaning the restoring force driving the oscillatory motion is proportional to the displacement (Povey, 1997a). Despite the translation of energy and the progressively moving profile of the wave, there is no net displacement of the medium (Williams, 2012).

2.3.2 Frequency

The frequency (f) of an ultrasonic wave is its defining characteristic and is typically expressed in units of MHz ($10^6\text{ s}^{-1}$). Frequency describes the number of compression waves produced per second, and is closely related to acoustic velocity, period, and wavelength via Equation 2.
The wavelength ($\lambda$) of a longitudinal compression wave is normally expressed in mm. When particle displacement is plotted as a function of distance, it describes the distance between the beginning of a rarified (low density) zone and the end of the successive compressed (high density) zone. Or more simply, the distance between any two identical points on sequential waves (Williams, 2012). Since ultrasonic waves exhibit higher frequencies, their wavelengths are small in comparison to audible sound waves.

The period ($T$) describes the time it takes for a particle to go from rest, to the point of maximum displacement, then back to resting position. It is most commonly reported in units of $\mu$s ($10^{-6} \cdot s$) for ultrasound. On a graph of displacement as a function of time, the period of the wave can be determined by finding the distance between two identical points on successive waves (Williams, 2012). As was the case with wavelength, period is inversely proportional to frequency. So ultrasonic waves tend to have short periods in comparison to audible sound waves.

![Graphical representations of wavelength and period](image-url)
2.3.3 Acoustic amplitude

Amplitude (a) describes the height of the wave, and corresponds to the magnitude of the pressure difference between compressed and rarified zones of the media, the maximum displacement of its particles, and the “strength” of the wave (Williams, 2012). When referring to audible acoustic waves, the amplitude determines how loud a sound is, and is commonly represented using the logarithmic unit decibels (dB), which relates acoustic pressure to a reference value. In SI units, amplitude is usually expressed in volts (V).

2.3.4 Acoustic velocity

Acoustic velocity (v) is governed by the thermodynamic properties of the medium through which it is translating. Based on the concept that sound is propagated as a harmonic longitudinal compression wave, the Newton-Laplace equation presents acoustic velocity through a given medium as a function of its bulk modulus (β) and density (ρ) (Ament, 1953; Urick, 1947; Wood, 1941).

\[ v = \sqrt{\frac{\beta}{\rho}} = \frac{1}{\sqrt{\rho K_s}} \]  \hspace{1cm} (3)

If bulk modulus and density data are available, values for acoustic velocity can be predicted for different media using Equation 3. Likewise, the equation can be used to draw conclusions about a fluid’s density and isentropic compressibility (the reciprocal of bulk modulus) from experimentally obtained values of acoustic velocity. However, Equation 3 is valid only when dealing with homogenous fluids. To draw accurate predictions or conclusions for non-homogeneous mixtures, such as emulsions, the equation must be modified to account for both phases of the medium. The
modification includes substituting the effective density and effective bulk modulus for \( \rho \) and \( \beta \), respectively. The resulting relationship is known as the Urick Equation, and can be seen below as Equation 4 (Povey, 1997a; Kuster & Toksöz, 1974; Urick, 1947).

\[
\nu = \sqrt{\frac{\sum_{i=1}^{n} \phi_i \beta_i}{\sum_{i=1}^{n} \phi_i \rho_i}}
\]  

(4)

Where \( \phi_i \) is the volume fraction of component \( i \) in the non-homogeneous mixture.

Kuchhal et al. (1997) investigated the Newton-Laplace equation’s validity in pressurized liquids by employing techniques that allowed them to calculate specific molar volume from ultrasonic parameters and comparing the calculated values to those from literature. Despite having consistently positive error between 5 and 10%, they concluded that the overall agreement between literature and experimental values was satisfactory. Jiu-Xun et al. (2006) refuted these conclusions, stating that the Newton-Laplace equation underestimates the acoustic velocity at high pressures. They went on to develop a modified equation that is suitable for use at such pressures.

\[
\nu = \frac{\nu_s}{\nu_0}
\]  

(5)

Where \( \nu_s \) is the adiabatic speed of sound, and \( \nu_0 \) is \( \nu_s \) at zero pressure condition.

Although usually expressed as a singular quantity under the adiabatic assumption (Bohn, 1988), two different types of ultrasonic velocity can be measured in a given attenuating media. These quantities are known as group and phase velocity. Group velocity describes the velocity of the entire envelope of an ultrasonic signal, whereas phase velocity describes the velocity of a single frequency component of the periodic wave (Laugier & Haïat, 2011; Wear, 2000). Group and phase velocity can be calculated via Equation 6 and Equation 7, respectively.
Equation 6: Group velocity as a function of frequency and wavelength

\[
v_g = \frac{d\omega}{dk} = \frac{d[2\pi f]}{d[\frac{2\pi}{\lambda}]} = \frac{df}{d[\frac{1}{\lambda}]}
\]

Equation 7: Phase velocity as a function of frequency and wavelength

\[
v_p = \frac{\omega}{k} = \frac{2\pi f}{2\pi} = f\lambda
\]

Since group velocity is concerned with the translation of the entire signal, it is represented by the speed at which information or energy is translated through the media. Group velocity is therefore directly observable and is the quantity most often reported in articles citing sound velocities (Povey, 1997a; Deschamps & Bescond, 1995). Conversely, phase velocity is not directly measurable rather it must be calculated using complex instrumentation and broadband ultrasonic pulses. Another notable difference in phase velocity is that it is dependent upon frequency in highly attenuating media due to pulse shape change during propagation via frequency-dependent attenuation and scattering (Haïat et al., 2006; Ragozzino, 1981).

2.3.5 Isentropic compressibility

Isentropic compressibility (\(\kappa_S\)), also known as adiabatic compressibility, is the reciprocal of the bulk modulus of elasticity (\(\beta\)). It describes the capability of a substance to undergo a reversible change in volume when subjected to hydrostatic pressure. More specifically, it is the rate of change in volume with respect to pressure, and can be calculated via Equation 8.

\[
\kappa_s = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S
\]

Compressibility is the characteristic of a liquid that facilitates ultrasonic wave propagation via longitudinal waves. The compressible nature of the fluid allows for the high density zones to be
created via compression, and the fact that the fluid’s compressibility is finite is what causes particles to return to their relaxed position (Dukhin & Goetz, 2010).

\[ \kappa_s = \frac{1}{v^2 \rho} \]  

(9)

Isentropic compressibility is indicative of the intermolecular forces present in a liquid; less compressible fluids exhibit stronger intermolecular forces. The isentropic compressibility can be determined experimentally by rearranging the Equation 3, as shown above in Equation 9.

2.3.6 Acoustic impedance

Acoustic impedance (Z) describes how the particles in a fluid respond to the propagation of a compression wave, such as ultrasound. Qualitatively, it is the amount of resistance a fluid applies to the propagation of the wave and quantitatively is the ratio of excess pressure to particle velocity. In a fluid composed of densely packed particles with strong intermolecular forces, ultrasound requires greater excess pressure to displace the particles than it would in a fluid with loosely packed particles and weak intermolecular forces. Therefore, the first substance would exhibit higher acoustic impedance (Gibbs et al., 2009).

The particle velocity used in this definition, however, must be distinguished from the aforementioned acoustic velocities; particle velocity \( (u_p) \) is the actual velocity exhibited by particles as they are displaced from their resting position whereas acoustic velocity refers to the speed at which the wave itself is propagated. An alternative method of computing acoustic impedance is via the product of the speed of sound and the density of the fluid (Laugier & Haïat, 2011). Both methods can be seen below in Equation 10.
\[
Z = \frac{P_e}{u_p} = \rho v
\] (10)

When an ultrasonic wave passes through an interface separating media with differing acoustic impedance, a portion of the energy is reflected back while the remainder continues to propagate through the second medium. The degree of reflection depends on amplitude reflection coefficient \((R_A)\) and can be calculated via Equation 11 (Gibbs et al., 2009; Dukhin & Goetz, 2010).

\[
R_A = \frac{I_R}{I_T} = \frac{(Z_1 - Z_2)^2}{(Z_1 + Z_2)^2}
\] (11)

Where \(I_R\) and \(I_T\) are the reflected and transmitted signal intensities, respectively.

The principle of reflection due to change in impedance is the principle that ultrasonic imaging relies upon. Values of \(R_A\) between most bodily tissues are around 1%, however between air and tissue the \(R_A\) usually exceeds 99%. This high degree of reflection minimizes the amount of energy transmitted into the tissue, thereby preventing ultrasound from penetrating to detect deeper structures. This phenomenon is called “dazzling” and is prevented by coating the surface of the tissue with a mineral oil based jelly to ensure there is no air between the device and the tissue (Williams, 2012).

2.3.7 Acoustic attenuation

Acoustic energy is diminished exponentially with distance as it travels from its source. This phenomenon presents as a decreased signal amplitude as path length increases and is referred to as acoustic attenuation. Attenuation is usually reported using the attenuation coefficient \((\alpha)\), which has units of dB⋅cm\(^{-1}\) or simply cm\(^{-1}\). In practice, this figure can be computed using the experimental and initial (or reference) values of amplitude, intensity, or pressure via Equation 12 (Szabo, 2004).
Equation 12: Attenuation coefficient from signal amplitude and a reference amplitude

\[ \alpha = \frac{1}{d} \ln \left( \frac{A_{ref}}{A} \right) = \frac{1}{d} \ln \left( \frac{P_0}{P} \right) = \frac{1}{d} \ln \left( \frac{I_0}{I} \right) \] 

Where \( d \) is the path length from transmitter to receiver (use 2\( d \) for pulse-echo techniques)

Attenuation occurs as the result of several different mechanisms including reflection (A), refraction (B), absorption (C), and diffraction (D), which are depicted in Figure 5.

Figure 5: Different sources of acoustic attenuation (Martin et al., 2015)

Reflection occurs when an ultrasonic wave passes through an interface between two liquids of differing acoustic impedances, as described in the previous section. These interactions are what cause echoes in audible acoustic waves. Reflection can be either specular or diffuse. Specular meaning the angle of incidence will always equal the angle of reflection, this occurs when sound waves encounter smooth interfaces, such as liquid-liquid or gas-liquid interfaces. Diffuse reflection results in reflection in many different directions and occurs when the interface is rough or porous, for example suspended solids in a liquid mixture (Gibbs et al., 2009 ; Martin et al., 2015).
Refraction occurs when two criteria are met. The first is that a wave passes through an interface with an angle of incidence that is not perpendicular to the surface of the interface. The second is that the interface separates two fluids in which the ultrasonic velocities differ. The angle of refraction ($\theta_r$) can be calculated using the acoustic velocities of in both fluids, and the angle of incidence ($\theta_i$) via Snell’s law (Gibbs et al., 2009; Dukhin & Goetz, 2010).

$$\theta_t = \sin^{-1} \left( \frac{v_2}{v_1} \cdot \sin \theta_r \right)$$

(13)

In ultrasonics, scattering occurs in all heterogeneous media and it describes any process that transforms the mode of motion of energy through said media. Scattering is usually the result of interaction with foreign bodies (reflectors) such as suspended solids or agglomerations of microbubbles. The definition of scattering does not require that the amount of energy is diminished, therefore phase change is also considered scattering. When this type of scattering occurs, that is without dissipation of energy, it is called forward scattering. However, scattering is almost always accompanied by energy depletion (Gibbs et al., 2009; Povey, 1997b).
For scattering to occur, the reflector must have a diameter equal to or smaller than the wavelength of the ultrasound. When the reflector is larger than the wavelength reflection occurs (Laugier & Haïat, 2011). When wavelength and reflector size are comparable diffuse scattering results in waves propagating with many different trajectories. If the interference is significantly less than the length of the wavelength Rayleigh scattering is observed. This entails equal scattering in all directions. The condition for Rayleigh scattering in terms of reflector radius (r) and wavelength (λ) is given by (Papadakis, 1965; Sboros et al., 2007; Povey, 1997b).

\[
\frac{2\pi r}{\lambda} < \frac{1}{10}
\]  

Equation 14: Rayleigh scattering condition

In homogeneous systems, attenuation is almost entirely due to acoustic energy absorption. Wherein ultrasonic energy is converted to another form, most commonly thermal energy. Several different characteristics of a medium can impact the amount of signal absorption. The properties that influence a medium’s propensity to absorb acoustic energy are thermal conductance and viscosity. The effects of thermal conductance are proportional to the ratio of the medium’s specific heat capacities (\(C_p & C_v\)). Since in liquids these values are nearly identical, the thermal effects of absorption can be assumed to be negligible. Therefore, ultrasonic attenuation in homogeneous liquids is essentially solely dependent upon viscosity. Attenuation due to viscous effects can be calculated for homogeneous liquids using an adaptation of Stokes Law (Dukhin & Goetz, 2009).

\[
\alpha = \frac{\omega^2}{3\rho v^3} \left[ \frac{4}{3} \eta + \eta^\nu \right]
\]

Equation 15: Stoke’s law of sound attenuation modified to account for bulk viscosity

Where \(\eta^\nu\) is the volume (bulk) viscosity of the media

Volume viscosity, also known as bulk viscosity (Morse & Ingard, 1986) or expansion coefficient of viscosity (Temkin, 1981), is a fluid property that becomes relevant to fluid dynamics when
compressibility of a substance cannot be ignored. Propagation of ultrasound is one of these cases. According to Temken (1981) bulk viscosity describes a fluids propensity to relax rotational and vibrational degrees of freedom, just as dynamic viscosity describes the relaxation of translational motion.

2.4 Existing and Emerging Ultrasonic Applications

2.4.1 Liquid density measurement

Adamowski et al. (1995) devised a system wherein density of a liquid could determined from experimental values of reflection coefficient between the unknown liquid and a fully defined stock solution (buffer rod), and propagation velocity through the combined matrix.

\[
R_A = \frac{I_R}{I_T} = \frac{(Z_1 - Z_2)^2}{(Z_1 + Z_2)^2} \quad (11)
\]

\[
Z_2 = \frac{Z_1(1 + R_A)}{1 - R_A}
\]

\[
\rho_2 = \frac{\rho_1 c_1 (1 + R_A)}{c_2 (1 - R_A)} \quad (16)
\]

This method was determined to be accurate in static and mobile liquids, within ±1% error of literature values. However, it was reported that when cavitation occurs the results became inconsistent. It is also noted that in order to make accurate measurements over a broad temperature range, the attenuation correlations for the buffer rod must be further developed, as the current model is only reliable at SATP (Adamowski et al., 1995).

In a paper by Bamberger & Greenwood (2004a) techniques similar to those implemented by Adamowski (1995) were employed to determine the density of kaolin clay slurries. Since the clay is insoluble in water, the solids concentration can be computed via Equation 17.
where $w$, $s$, and $p$ denote water, slurry, and particle, respectively.

A more recent paper by Hoche et al. (2015) used similar techniques to measure densities and associated acoustic velocities of a ternary water-maltose-ethanol system. Error in density, specific acoustic impedance, and reflection coefficient were reported as $\pm 0.12\%$, $\pm 0.12\%$, and $\pm 0.15\%$, respectively. Cited sources of error included poor temperature control, and low signal resolution from a 50MHz ultrasound.

Papers by Daridon et al. (1998) and by Lagourette & Daridon (1999) demonstrate techniques to determine density and compressibility of heavy synthetic cuts and petroleum fractions, respectively, over a range of temperatures and pressures. Both papers opt to employ empirical correlations instead of using reflection coefficients, as with the previous two papers.

2.4.2 Search units

Ultrasonic search units are based on the concept of echo-location, which are observed in nature by animals including bats, whales, and dolphins. When an ultrasonic wave is produced in a well-defined medium, the time-of-flight (TOF) and amplitude can be used to determine how far away a reflector is. Prakash et al. (2014) developed a self-calibrating system for monitoring oil-water interfaces, as well as emulsions, in tanks or desalters. The technique employs a pulse-echo sensor with a fixed reflector that is a known distance from the transducer. Therefore, based on the TOF of the initial signal, the acoustic velocity in fluid the first fluid can easily be determined. The next realized signal would be due to reflection from the interface under investigation. Since the velocity in the fluid is now known, the distance can be computed (Prakash et al., 2014).
Additional information about a detector can be deduced by analyzing more involved ultrasonic parameters, such as phase mode and diffraction pattern. Acciani et al. (2010) and Amjad et al. (2015) both proposed techniques for detecting and quantifying superficial damage to buried pipelines using measurements of ultrasonic parameters. The method proposed by Amjad et al. demonstrated the capability of detecting and providing quantitative information about the superficial size of hole type defects with diameters between 3.25 mm and 6.35 mm (Amjad et al., 2015). By employing more sophisticated analysis of the ultrasonic data, Acciani et al. was able to draw conclusions about the axial and angular size of the defects (Acciani, 2010).

2.4.3 Particle sizing

As mentioned in a previous section, optical analysis techniques employ scattering and diffraction to determine particle size. A review of the literature revealed several methods of producing analogous ultrasonic technology that estimate size based on ultrasonic scattering (McClements, 1996; McClements & Povey, 1989; Alba, 1992). However, despite much advancement in this technology, velocity and attenuation correlations have been shown to provide more accurate data in both suspended solids and emulsions (Povey, 1997c).

A report by Sayan & Ulrich (2002) demonstrates acoustic velocity’s dependence upon particle size and suspended solids concentration. This idea was further expanded on by Shukla & Prakash (2006), who were able to accurately characterize two- and three-phase slurries in terms of particle size and concentration. The average uncertainty for particle size was reported as less than ±3µm. The slurries were prepared using 34 and 110µm particles and their binary mixtures in distilled water, with a concentration range of 2-10% by volume, and superficial gas velocity of 0.03-0.10m/s in the three-phase slurries.
Other techniques for characterizing slurries of suspended solids, such as those reported by Stolojanu & Prakash (2001) employ both velocity, attenuation, and mean frequency analysis. The particles used in this study included sizes of 35, 70, and 180µm with solids loading up to 45%. Empirical correlations were developed from the data, from which it was determined that solids concentration could be indicated by velocity between 10-50% solids by volume. While at lower concentrations variation between attenuation and peak frequency gave a better estimate. In terms of particle size distribution, attenuation showed a strong relationship but estimates are best made using velocity data and a plot of peak frequency as a function of acoustic velocity.

Bamberger & Greenwood (2004b) further displayed the power of attenuation analysis by demonstrating that attenuation data alone can be used to measure slurry concentration. In their report, Bamberger & Greenwood use real-time measurements of attenuation to monitor the process of slurry mixing via single sensor and sensor arrays. The correlations between ultrasonic measurements and concentration were statistically not different from those prepared by extractive techniques. Thus proving that real-time ultrasonic monitoring is a viable option for measuring slurries concentration on-line.

2.4.4 Liquid characterization

The determination of atomic chain length is of great importance in the polymer industry and in other industries concerned with chemical identification. An ultrasonic method of investigating this parameter was proposed in an article by Povey et al. (2005). The proposed technique models ultrasonic velocity measurements and compressibility values as a function of carbon (or silicon) chain length in primary alcohols, n-alkanes, and polydimethylsiloxanes (PMDS) of varying chain length. The experimental data was compared to data calculated via a modification of the Urick equation, which can be seen in Equation 18.
\[ v = \frac{\sum_{i=1}^{n} \phi_i \beta_i}{\sqrt{\sum_{i=1}^{n} \phi_i \rho_i}} \]  
\[ v = \frac{1}{\sqrt{\sum_{i=1}^{n} \phi_i \kappa_i \cdot \sum_{i=1}^{n} \phi_i \rho_i}} \]  
\[ v = \frac{1}{\sqrt{\sum_{i=1}^{n} \phi_i \kappa_i + n_e \phi_e \kappa_e \cdot \sum_{i=1}^{n} \phi_i \rho_i + n_e \phi_e \rho_e}} \]  
\[ v = \frac{1}{\sqrt{(n - n_e) \phi_e \kappa_e + n_e \phi_e \kappa_e) \cdot ((n - n_e) \phi_e \rho_e + n_e \phi_e \rho_e)}} \]  

Equation 18 was found to be accurate in PMDS from C/S = 2 – 667, whereas in primary alcohols and n-alkanes it failed until the chain lengths reached a critical value (5 for alcohols and 9 for alkanes). Limitations of this study are that it can not be used unless the nature of the liquid is known (Povey, 2005).

A paper by Henning et al. (2000) proposed an instrument (Fluid Analyzer US 2100) for on-line ultrasonic technique for concentration measurement of complex liquids. The instrument is a dip-in sensor equipped to take measurements of acoustic velocity, impedance and attenuation. It was designed for applications in both the chemical and food industry, with an emphasis on high quality chemical production and separation. The technique is based on acoustic impedance correlations with amplitude and absorption. Numerical methods, specifically successive approximation, are used to compute concentration values via a series of involved calculations which are fully cataloged in the paper (Henning, 2000).
2.5 Conclusions

Within the reviewed literature, ultrasonic inspection has been demonstrated as a powerful tool for analysis in a wide range of industrial applications. In some of these, conventional methods of analysis are able to provide greater accuracy, for example GC-MS for mixture characterization, or LD for particle sizing, or conductivity for salinity analysis. However, these methods have noted shortcomings that make them unsuitable for many applications, including high cost, retention time, and medium incompatibility. The versatility and robustness of ultrasonic techniques make them ideal alternatives for on-line process monitoring.
2.6 References


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http://www.sengpielaudio.com/calculator-amplitude.htm


Chapter 3: Development of ultrasonic techniques for characterization of hydrocarbon mixtures

3.1 Introduction

Energy demands in Canada are on the rise, and a major contributor to this phenomenon is the growing demand for transportation fuels and other petroleum products. The detrimental effects that fossil fuels have on our health and the environment are well documented and undeniable. However, it is unreasonable to suggest that Canadians can solely rely on renewable resources without significantly impairing their quality of life. A more reasonable approach to mitigating the risks associated with fossil fuel use is to ensure that harmful components such as aromatics, sulfur compounds and particulates are kept within their acceptable concentration limits. Since some of the aforementioned components can cause issues in the refining process, the ability to detect unacceptable concentration levels in real-time is invaluable.

With the current price of oil, and general financial climate surrounding the petroleum industry in North America, many refiners and traders opted to hold products in storage, deferring its sale until a later date (EIA, 2016, p. 44). This has resulted in historically high crude oil inventories, reaching 1.227 Billion Barrels as of June 6th 2016 (EIA, 2016, p. 4) in the U.S. alone. When stored in static holding tanks, crude oil often tends to separate into layers of varying density and volatility. When a mixture undergoes such separation, the risk of losing valuable light ends increases dramatically. Currently there is no standardized method of monitoring said losses, and conversations with engineers from industry suggest that a robust monitoring technique would be of great interest. If significant amounts of light ends are lost, the physical properties of the remaining crude oil mixture will undoubtedly change. For example, the average density of the crude mixture should increase with the amount of light-ends lost, as the lighter ends generally have much lower densities. Since
physical properties such as density and compressibility dictate the speed of sound, ultrasonic monitoring could potentially be used to detect said losses.

Desirable traits for the equipment intended to satisfy the needs described above include that it be; robust, compact, non-destructive, minimally invasive, and able to report results in real-time. This paper outlines preliminary research that demonstrates the feasibility of ultrasonic monitoring for these purposes.

Currently, the accepted method for determining what types of hydrocarbons are present in a mixture is by gas chromatography-mass spectroscopy (GCMS) (CEPA Environmental Registry, 1997), an analytical method for testing concentrations of volatile, thermally stable compounds. While GCMS provides high resolution power, leading to very accurate results, it does have other drawbacks that make it unsuitable for the discussed purposes. The most notable issue is that GCMS does not sample continuously, rather it is used to measure small samples periodically. Since the retention time of these samples can be several minutes long, measurements cannot be made in real-time. This is an issue because by the time the gas chromatograph is able to detect an abnormally high concentration of aromatics (or other undesirable compound), it could be too late to address the problem. Thus GC is appropriate for monitoring final product composition to ensure government regulations are being met, but is not effective for monitoring feed stock or intermediate products. Other similar techniques such as high performance liquid chromatography (HPLC) or atomic absorption spectroscopy (AAS) have similar drawbacks. It should also be noted that these kinds of machines employ destructive analysis techniques, meaning that the sample is destroyed during analysis. Samples are generally very small, so the overall impact on production would be negligible but it is still worth noting.
The use of ultrasonic wave parameters has proven to be an effective means of monitoring liquids online. This is largely due to the speed of sound’s dependence on the physical and thermodynamic properties of the medium through which it is propagating (Kiełczynski, et al., 2014). Bamberger and Greenwood (2002) report that ultrasonic parameters, such as acoustic velocity and attenuation can be used to determine the viscosity of fluids and slurries. Another paper demonstrates that the same parameters can be used to determine density and suspended solids concentration in the same types of mixtures (Greenwood, et al., 1999). Ultrasonic techniques have even been used to estimate the atomic chain length of certain hydrocarbons, including primary alkanes, 1-alcohols and some polymers (Povey, et al., 2005).

3.2 Project outline and objectives

Ultrasonic techniques possess all of the previously mentioned desirable qualities for a monitoring system. The analysis is non-destructive and minimally invasive, hardware can be compact, the results are robust and reliable, and most importantly, data can be seen in real time. When considering all of these traits and comparing ultrasonic techniques to the previously discussed methods, it is clear that ultrasonics are an ideal choice for liquid mixture monitoring. Therefore, the objective for this project is to develop a method of monitoring liquid mixtures for changes in composition in real time, using measurements of ultrasonic parameters.

The first steps in developing this method will largely involve observing and accounting for differences in the behaviour of ultrasonic parameters, such as acoustic velocity and attenuation in different liquids. Initial experiments will employ n-alkanes of various chain lengths, iso-alkanes, cycloalkanes, aromatics, paraffin oils, and crude oil. Using liquids with such diverse physical properties and chemical structures will allow for a better understanding, and more complete picture of ultrasonic wave behaviour. Using experimental values of density and acoustic velocity,
isentropic compressibilities of the aforementioned liquids will be computed and analyzed for correlations with molecular size. The ideal outcome being that paraffinic hydrocarbons yield significantly different correlations than those observed in aromatics etc. This will provide a basis by which different liquids can be distinguished experimentally and thus aid in detection and characterization.

3.3 Basic theory
Consider two transducers; a transmitter and a receiver, both submerged in a liquid medium and separated by a fixed distance, \( d \). If an ultrasonic wave is produced at the transmitter and subsequently detected by the receiver, the time it took for the signal to be picked up is known as the time of flight (TOF). The distance between the transducer and the receiver, along with the TOF can then be used in Equation 19 to calculate the speed of sound in the given medium.

\[
v = \frac{d}{TOF}
\]  

(19)

Sound propagates through media as compressional waves. This is accomplished via alternating compression and rarefaction of the media in question. Since displacement caused by the passage of the acoustic waves is infinitesimally small, it can be safely assumed to be harmonic in nature. Equations based on this concept, such as the Newton-Laplace equation, model acoustic velocity as a function of the isentropic compressibility and density of the medium through which sound is propagating. This relationship can be seen Equation 20 (Ament, 1953; Urick, 1947).

\[
v = \frac{1}{\sqrt{\kappa_s \rho}}
\]  

(20)

Where \( \kappa_s \) is the isentropic compressibility of the fluid and \( \rho \) is the density
By rearranging Equation 20, experimental values for acoustic velocity and density can be used to determine the isentropic compressibility of a given fluid. Compressibility refers to a fluid’s ability to compress thereby reducing its specific volume when subjected to an external force. Isentropic compressibility specifically refers to the ratio of volume change to external pressure when entropy is held constant. By determining compressibility, a better understanding of the driving forces behind ultrasonic interactions can be achieved.

Another parameter that can readily be calculated using velocity and density is acoustic impedance, which quantifies the medium’s resistance to acoustic pressure (Kinsler et al., 2000).

\[ Z = v\rho \]  \hspace{1cm} (21)

The second measured ultrasonic parameter that was collected was signal amplitude. Using this the coefficient of attenuation of a given fluid was calculated. Attenuation describes the rate at which acoustic energy is diminished as a result of propagation through a given medium. Attenuation mainly takes place as the result of two different mechanisms; scattering and absorption. Scattering describes a situation where the wave begins to propagate in a direction other than its original trajectory, and is usually the result of interactions with gas-liquid or liquid-liquid interfaces, or with dispersed solids in a heterogeneous mixture. Absorption is essentially the only contributor to attenuation in homogeneous systems, and it is caused by the conversion of sound energy into other forms of energy. Most absorption is the result of viscous forces acting on the sound wave and can be calculated for homogeneous liquids using an adaptation of Stokes Law (Dukhin & Goetz, 2009).

\[ \alpha = \frac{\omega^2}{3\rho v^3} \left[ \frac{4}{3} \eta + \eta^v \right] \]  \hspace{1cm} (22)

Where \( \eta^v \) is the volume (bulk) viscosity of the media.
The attenuation coefficient, \( \alpha \), can be calculated experimentally via Equation 23, using the ultrasonic path length, the amplitude of a given signal and the amplitude of a reference signal.

\[
\alpha = \frac{1}{d} \ln \left[ \frac{A_{\text{ref}}}{A} \right]
\]  

Values for attenuation coefficient are indicative of droplet size distribution and dispersed phase volume fraction (Basaran et al., 1998). This information could be useful for characterizing emulsion layers in crude oil desalters. Attenuation coefficient can also be indicative of gaseous volume fraction dispersed in a liquid matrix (Fahy, 2001). These correlations are beyond the scope of this paper, but will be considered when studying emulsions in the future.

In order to use these two parameters to draw conclusions about a medium with confidence, responses to varying conditions must be investigated thoroughly. In this experiment variations in acoustic velocity and attenuation coefficient will be tested for correlations with changes in temperature and media composition. Understanding how these parameters behave in response to different types of media manipulation will provide preliminary information for more detailed investigation in the future.

### 3.4 Experimental apparatus

Ultrasonic wave parameters were tested over a range of temperatures and through different media, of varying compositions. The vessel used to contain the medium under observation was a 1800mL jacketed glass tank. According to Adamowski et al. (1995) ultrasonic measurements of acoustic velocity were not affected by flow rate, as long as cavitation was not present. This means that the stationary model used in this experiment can adequately represent an industrial setting.
To regulate the temperature of the media, a PolyScience temperature controller, also known as a water box, fed water to the heated jacket. To maintain a uniform temperature profile throughout the liquid, a vertical agitator stirred the contents of the tank. Fixed to the vessel was a type K thermocouple, which was used to monitor the temperature of the fluid. A detailed schematic of this set up can be seen below in Figure 7.

![Figure 7: Schematic of experimental set up](image)

A probe specifically designed for this project was supported by a fixed stand, which allowed it to be partially submerged in the liquid. The probe was equipped with two transducers, a 1.5MHz ultrasonic wave transmitter and a receiver fixed with ~5 cm of separation between them. A detailed scale diagram of the probe can be seen in Figure 8.
The probe was connected to a UT340 pulse receiver by UTEX Scientific Instruments Inc. The pulse receiver sent signals to the transducer to produce an ultrasonic wave train, generating a pulse at a rate of 20kHz, or every 50µs. The unit was also responsible for receiving the ultrasonic signals from the receiver transducer. Received signals were plotted on a plot of voltage vs. time using software called InspectionWare 64. From this signal peaks provided time of flight and amplitude data. Peaks had a width of <2ns, which for reference, is approximately 0.0057% of a 35µs time-of-flight. This equipment can be seen as a part of the set up in Figure 7, while an example of the signal produced by the wave can be seen in Figure 9.
The strength of the received signal can be determined by the height of the peak in relation to the Y-axis, which has units of volts. This information is important when studying the implications of the attenuation coefficient through a specific medium. The time of flight a signal is the time it takes the ultrasonic wave to move from the transmitter to the receiver. This can be determined by inspecting where the major signal peak shows up in relation to the X-axis, which is in units of microseconds. The fact that the transmitter and receiver are a fixed distance apart makes calculating experimental acoustic velocity very simple, using Equation 19.

The density of each pure sample was tested using an Eagle Eye SG-Ultra Max Digital Hydrometer/Density Meter. Determining values for mass density will allow for calculation of isentropic compressibility, and for correlations to be made with ultrasonic wave parameters. This will aid in enabling distinction between media of different compositions. A photo of the Density meter can be seen in Figure 10.
3.5 Materials and methods

The liquids under observation include 4 different n-alkanes varying between 6 and 12 carbons in length, isohexane, cyclohexane, isooctane, toluene, paraffinic mineral, oil and crude oil. The n-alkanes serve as a baseline for ultrasonic behaviour in paraffinic hydrocarbons, while the mineral oil allows us to test whether longer paraffins follow similar trends, as well as to study the effects of density and chain length on ultrasonic behaviour. Tests done in other types of alkanes and toluene provide some insight as to how bonding, structure, and polarity affect the parameters under investigation. The paper also investigates the effects of concentration on hydrocarbon mixtures; including simple binary hydrocarbon mixtures and varying concentrations in complex blends like crude and mineral oils. The results of these tests provide insight as to whether ultrasonics can be employed to detect major fluctuations in sample concentration, or to detect losses over time. Detailed information about each liquid used in this paper is listed below in Table 1 below.
Table 1: Materials

<table>
<thead>
<tr>
<th>Substance</th>
<th>Supplier</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>VWR Analytical</td>
<td>GC-98%</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>Alfa Aesar</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>Alfa Aesar</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>Alfa Aesar</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>Anachemia</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>isoHexane</td>
<td>Emsure</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>isoOctane</td>
<td>Emsure</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>Toluene</td>
<td>BDH</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>Anachemia</td>
<td>Paraffin Oil, Coloured White</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>Imperial Oil</td>
<td>Coker Crude</td>
</tr>
<tr>
<td>Hexanes</td>
<td>Caledon</td>
<td>&lt;60% n-Hexane, &gt;95% Hexane</td>
</tr>
</tbody>
</table>

Sampling techniques for the experiment remained uniform throughout the entire experiment. Data was collected over 10 seconds at a sampling frequency of 100Hz, yielding 1000 values of time-of-flight and amplitude per run. The arithmetic average of each set of values was calculated and subsequently used to calculate acoustic velocity and attenuation, respectively. The standard deviation of each set was also calculated to ensure the data was reasonably consistent.
3.6 Results and discussion

3.6.1 Measurements in paraffinic hydrocarbons

The first series of experiments were conducted in n-alkanes with carbon numbers in the range of 6 to 12. The effects of carbon chain length and temperature on acoustic velocity were investigated, with temperatures varying from 25 to 60°C. Figure 6 shows that at a given temperature higher acoustic velocities are observed in n-alkanes with higher carbon numbers. It is also noted from the figure that within these parameters, acoustic velocity decreases as temperature increases. Measurement error for this data ranges between ±0.26 to ±0.32m/s.

![Graph showing velocity in n-alkanes as a function of chain length](image)

Figure 12: Velocity in n-alkanes as a function of chain length

Since an increase in carbon number yields alkanes with higher densities, according to the Newton-Laplace equation, longer carbon chain lengths should facilitate lower speeds of sound. The observed trends do not agree with this pattern, and therefore indicate that compressibility is negatively correlated with carbon number.

\[
v = \frac{1}{\sqrt{\beta_s \rho}}
\]  

(20)
To better visualize the relationship between temperature and acoustic velocity the data from Figure 12 was plotted as a function of temperature for each n-alkane.

![Figure 13: Acoustic velocity in n-alkanes as a function of temperature](image)

The observed negative correlation between temperature and acoustic velocity supports the notion that isentropic compressibility must be treated as a dynamic parameter. Since an increase in temperature results in reduced density, which once again, according to the Newton-Laplace equation should increase the observed speed of sound. Deviation from this expectation indicates that the rate-of-change in isentropic compressibility with respect to temperature (and carbon number) is opposite in sign and greater in magnitude when compared to the associated rate-of-change in density. That is to say that when temperature is increased, compressibility increases more than enough to compensate for the drop in the fluid’s density.

It can also be observed from Figure 13 that the relationship between temperature and velocity is linear within the scope of this experiment. Linear models for each liquid were prepared using statistical software called Origin.
During the experiments, density data for each liquid was obtained using a density meter (Eagle-Eye SG-Ultra Max). Readings were taken over a temperature range of 25-70°C with the exception of n-hexane. The temperature range for n-Hexane was shifted to 22-60°C to avoid problems that may arise from phase-change, which occurs around 68°C (Haynes, 2014, pp. 3-282).

The resulting data was plotted as a function of temperature and fit with the following linear model:

\[ \rho(T) = A \cdot T + B \]  

(25)

The Newton-Laplace equation can be rearranged to solve for isentropic compressibility:

\[ \kappa_s = \frac{1}{V^2 \rho} \]  

(26)

Using the above relationship with the temperature dependent equations for density and velocity, compressibilities can be modelled as a rational function with a third degree polynomial in the
denominator. This relationship however, is overly complicated and is adequately represented by a second degree polynomial

\[ \kappa_s(T) = AT^2 + BT + C \]  \hspace{1cm} (27)

![Graph showing isentropic compressibility of n-alkanes as a function of temperature](image)

Figure 15: Isentropic compressibility of n-alkanes as a function of temperature

Figure 15 shows that isentropic compressibility increases with temperature and decreases with chain length for each of the n-alkanes tested. This can be explained by the variation of intermolecular forces with respect to molecular size; The only type of intermolecular forces present in n-alkanes are a subclass of Van der Waals forces, called London dispersion (or simply dispersion) forces. Dispersion forces are weak attractive forces facilitated by momentary dipoles present in polar and non-polar molecules. These forces are enhanced by larger atoms because the valence electrons are generally further from the positively charged nucleus, and are therefore more easily polarized into an instantaneously temporary dipole. Longer molecules also have an enhancing effect on dispersion forces because their length can facilitate larger temporary dipoles.
Larger molecules yield higher intermolecular forces, which make a liquid more “rigid”. These rigid liquids can facilitate translation of compression waves more quickly than liquids with higher compressibility. To illustrate this phenomenon more effectively, the media facilitating the propagation of a compression wave can be compared to a frictionless spring constantly undergoing compression and rarefaction. In this example the bulk modulus (inverse of isentropic compressibility) can be compared to the spring constant (Ensminger & Bond, 2012). The higher the spring constant, the more rigid the spring and thus the faster it contracts and expands when undergoing harmonic motion.

While the effects of temperature on density and compressibility are opposite, they are the result of the same mechanism. As molecules in a liquid are heated they gain kinetic energy and thus begin to move faster and on average, are farther apart. This causes the liquid to occupy more space per unit mass, thus decreasing density. The increased separation between molecules also has an effect on the attractive and repulsive forces between the molecules, known as intermolecular forces. These forces become weaker as molecules become further apart, thus rendering the liquid more susceptible to deformation; thereby increasing compressibility.

It may be noted that while compressibility data provides some insights into the nature of liquid molecules and their interactions, it is estimated indirectly from acoustic measurements. For the purpose of identification of the liquid sample, it would be simpler to use directly measured parameters. It can be seen from Figure 12 that there is direct relationship between acoustic velocity and carbon number of n-alkanes. After fitting the data using different models, it was decided that a logarithmic model fit the data adequately and most consistently at each temperature.

\[ V(C) = A \ln C + B \]  
\[ (28) \]
Equation 28 can be rearranged to estimate carbon number of an n-alkane from measurement of acoustic velocity at a given temperature. This technique was used to predict carbon number of mineral oil samples which contained mixtures of paraffinic hydrocarbons. Acoustic velocities were measured at temperatures of 30 and 60°C in the oil samples. Figure 16 shows the that carbon number (average) of the paraffinic oil is about 19.75. This value is very close the value of about 20-21 obtained from GC-MS analysis of the oil samples.

![Graph showing acoustic velocity vs. carbon number](image)

Figure 16: Predicting carbon number from acoustic velocity at a given temperature

A second method to predict carbon number for mixture of alkanes based on compressibility was also developed. By obtaining experimental values for density and acoustic velocity, one could calculate compressibility and use said relationship to obtain an estimate of the average carbon number the liquid in real-time. To further investigate the strength of the correlation between chain length and isentropic compressibility to two parameters were compared graphically in Figure 17 below.
A power function was used to model the data points obtained at each temperature. The decision to use a power function over a polynomial was made based on the assumption that the curve would eventually be used for extrapolation. A second order polynomial, constructed by way of least squares method, would reach a minimum value just beyond $C=12$ before exhibiting a positive correlation between compressibility and chain length. Intuitively this would not make sense, as it has been determined that larger molecules exhibit higher intermolecular forces and thus lower compressibility values. The aforementioned power function can be seen below in Equation 29.

$$\kappa_s(C) = AC^B$$  \hspace{1cm} (29)

With the data separated into temperature specific groups, it is less useful for chain length approximation, as temperatures can vary and the curve of interest will likely lie somewhere between the ones shown in Figure 17. To avoid errors due to interpolation, the coefficients were modelled as functions of temperature. By doing this, carbon number can be predicted from
isentropic compressibility (using the power equation) for continuous values of temperature, rather than being restricted to a set of discrete figures.

![Graph showing Coefficient A and Coefficient B as a function of temperature](image)

**Figure 18:** Compressibility power coefficients as a function of temperature

The temperature dependent models for the power coefficients used to calculate carbon number from compressibility (depicted above) are summarized below.

\[
Coef(T) = \gamma T^2 + \delta T + \epsilon \tag{30}
\]

\[
C(\kappa_S, T) = \frac{\kappa_S}{1.20653T^2 + 6.7014T + 3256.5} \cdot \frac{1}{-4.5692 \times 10^{-5}T - 0.54298} \tag{31}
\]

Using Equation 13, a surface plot of carbon number as a function of isentropic compressibility and temperature was constructed. The resulting surface (shown below in Figure 19) can be used to interpolate carbon number from temperature and compressibility data, or if the carbon number was determined by other means, could be useful for determining whether or not a sample contains high concentrations of normal alkanes.
Figure 19: Carbon number of \( n \)-alkanes as a function temperature and compressibility

The efficacy of the above model was investigated for each alkane studied. This was done using compressibility values at \( T = (35, 45, 55) \)°C. Error was maximized to produce a “worst case scenario” estimate of the model’s accuracy by using temperatures halfway between the curves from Figure 17. The resulting values for carbon chain length were quite accurate and are tabulated with the corresponding error (as a percent of the true value) below in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>( n )-Hexane</th>
<th>( n )-Heptane</th>
<th>( n )-Nonane</th>
<th>( n )-Dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Error</td>
<td>Value</td>
<td>Error</td>
</tr>
<tr>
<td>( 35 ) Celsius</td>
<td>5.78</td>
<td>3.65%</td>
<td>7.11</td>
<td>1.62%</td>
</tr>
<tr>
<td>( 45 ) Celsius</td>
<td>5.80</td>
<td>3.29%</td>
<td>7.16</td>
<td>2.28%</td>
</tr>
<tr>
<td>( 55 ) Celsius</td>
<td>5.82</td>
<td>3.06%</td>
<td>7.20</td>
<td>2.88%</td>
</tr>
</tbody>
</table>
The proposed model for carbon number as a function of temperature and compressibility performed reasonably well in each of the n-Alkanes studied. For reference, experimental and literature values of acoustic velocity, mass density and isentropic compressibility for each of the n-alkanes studied are tabulated below in Table 3. In each instance, experimental values are consistent with values found in literature.

Table 3: Experimental and literature values of ultrasonic parameters for n-alkanes

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Acoustic Velocity (m/s)</th>
<th>Mass Density (kg/m³)</th>
<th>Compressibility (TPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-Hexane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1056.1</td>
<td>1056ᵃ</td>
<td>652.2</td>
</tr>
<tr>
<td>40</td>
<td>1010.2</td>
<td>1009.5ᵇ</td>
<td>641.5</td>
</tr>
<tr>
<td>50</td>
<td>964.77</td>
<td>630.8</td>
<td>631.9ᶜ</td>
</tr>
<tr>
<td>60</td>
<td>921.34</td>
<td>920.7ᵇ</td>
<td>620.1</td>
</tr>
<tr>
<td><strong>n-Heptane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1113.0</td>
<td>1113ᵃ</td>
<td>675.39</td>
</tr>
<tr>
<td>40</td>
<td>1069.4</td>
<td>1066.9ᵇ</td>
<td>666.21</td>
</tr>
<tr>
<td>50</td>
<td>1026.2</td>
<td>657.03</td>
<td>659.16ᵈ</td>
</tr>
<tr>
<td>60</td>
<td>983.90</td>
<td>982.9ᵇ</td>
<td>647.86</td>
</tr>
<tr>
<td><strong>n-Nonane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1186.1</td>
<td>711.32</td>
<td>709.69ᵉ</td>
</tr>
<tr>
<td>40</td>
<td>1145.5</td>
<td>1146.9ᵇ</td>
<td>702.13</td>
</tr>
<tr>
<td>50</td>
<td>1105.7</td>
<td>692.93</td>
<td>693.95ᵉ</td>
</tr>
<tr>
<td>60</td>
<td>1066.0</td>
<td>1068.7ᵇ</td>
<td>683.74</td>
</tr>
<tr>
<td><strong>n-Dodecane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1256.3</td>
<td>1260ᶠ</td>
<td>741.37</td>
</tr>
<tr>
<td>40</td>
<td>1217.1</td>
<td>1221.4ᵇ</td>
<td>733.20</td>
</tr>
<tr>
<td>50</td>
<td>1179.2</td>
<td>725.03</td>
<td>727.4ᵍ</td>
</tr>
<tr>
<td>60</td>
<td>1141.7</td>
<td>1147.8ᵇ</td>
<td>716.86</td>
</tr>
</tbody>
</table>

[a] (Oswal & Maisura, 2002)  [b] (Boelhouwer, 1967)  [c] (Alekerov, 1975)
[d] (Sagdev et al., 2013)  [e] (Ramos-Estrada, et al., 2011)  [f] (Gonzalez, et al., 2003)
[g] (Caudwell, et al., 2004)
3.6.2 Measurements in different hydrocarbon types

The different classes of hydrocarbons include cyclic, branched, and aromatic hydrocarbons. In this part of the investigations, 4 representative compounds from 3 different “classes” were selected and compared with n-alkanes of similar carbon number. These compounds included isohexane (2-methylpentane), cyclohexane, isoctane (224-trimethylpentane), and toluene (methylbenzene). Figure 20 compares the acoustic velocity measured in cyclohexane, toluene and iso-hexane with the values observed with n-alkanes.

![Figure 20: Acoustic velocity in hydrocarbons as a function of carbon number at 30°C](image)

The sampling methodology was similar to that of the previous section, with slight alterations. Isohexane was examined over a temperature range of 21.2 to 55°C to accommodate its low boiling point of ~60°C (Haynes, 2014, pp. 3-384), while toluene was only examined from 25-50°C because of a technical issue with the equipment. Data for iso-octane was collected from 25-60°C, but the data at 25°C was discarded as it was deemed unreliable due to another technical problem.
In the case of acoustic velocity’s response to variation in temperature, the hydrocarbons under investigation follow the same general trend as n-alkanes. Strong negative linear correlations were observed in each case. It should be noted however, that the velocities do not seem to have a specific trend with respect to carbon number as they did in the case of the n-alkanes. For example, Figure 21 shows cyclohexane facilitating much higher acoustic velocities than isoocatane, which contrasts the relationship observed between carbon number and acoustic velocity in n-alkanes. This suggests that structural isomerism has a significant effect on the acoustic velocity observed in alkanes. This relationship can be investigated by comparing the results in each of the 3 structural isomers of hexane under investigation, seen below in Figure 22.
Figure 21 shows that acoustic velocity measurements in isohexane (B) are much lower than the values observed in n-hexane (A). Whereas in cyclohexane (C), we observe much faster speeds of sound. Again, this can be attributed to varying strengths of dispersion forces exhibited by each isomer. Strength of dispersion forces are often said to increase with molecular weight, which is generally true when dealing with similarly shaped molecules. However, in this case it is the lightest of the three isomers, cyclohexane, that facilitates the fastest propagation of sound waves. Indicating that its associated dispersion forces are stronger than those of iso- and n-hexane.

Cyclohexane’s comparatively high dispersion forces can be attributed to its increased surface area and resistance to deformation. Both of which are products of its ring-like conformation. Cyclohexane’s resistance to deformation limits variation in molecular shape, thus facilitating close, lattice-like packing. Close packing combined with increased surface area, allows for increased overlap of electron clouds, which is conducive to greater attractive forces and thus results in a more rigid liquid. In contrast, n-alkanes have malleable or “floppy” structures, making them less suitable for close packing. The increased “void space” between molecules, along with the reduced surface area associated with linear conformations, inhibits overlapping of electron clouds and thereby reduces dispersion forces. Similar mechanisms, but to a greater extent, cause the further reduced intermolecular forces associated with isohexane. Its branched structure makes it very difficult to pack closely and vastly reduces the molecule’s surface area (Roberts & Caserio, 1977). The effects of branching on acoustic velocity are further exemplified in the case of isoctane, which has sound speed values similar to those found in n-hexane.

Of all the pure components investigated, toluene exhibited the highest acoustic velocity, which is likely resultant of its unique structure. Toluene exhibits similar physical characteristics of both cyclo- and isohexane. Like cyclohexane; the base shape of the molecule is ring-like, but like
isohexane; it contains a branched methyl group that may hinder close packing. However, the distinguishing characteristic of toluene’s structure is its aromaticity. The 6 carbon atoms that compose the phenol group in toluene are all sp² hybridized, whereas the branched methyl carbon is sp³ hybridized. The increased influence of the s orbital on sp² orbitals cause them to be more electronegative than their sp³ counterparts. In the case of toluene, the difference in electronegativity is enough to draw some electron density away from the methyl group and into the phenol ring. This causes a small permanent dipole moment of about 0.375 Debye (Sigma-Aldrich, n.d.). The permanent dipole in toluene make dipole-dipole interactions possible, however the effects of these interactions are limited because of the very small difference in charge across the molecule. Therefore, the dominating intermolecular forces in toluene are dispersion forces.

Densities for the aforementioned hydrocarbons were measured the same way as the n-alkanes were in the previous section. The data was then plotted in Figure 23 and used to construct linear, temperature dependent models of density for each liquid taking the form of Equation 25.

![Figure 23: Density of hydrocarbons as a function of temperature](image-url)
\[ \rho(T) = A \cdot T + B \] 

Density decreased linearly in the cyclic, branched and aromatic compounds as it did in the n-alkanes. Toluene has the highest density because of its planar shape, which is conducive to close packing. Additionally, the conjugated double bonds between carbon atoms are shorter than single carbon-carbon bonds, making the molecule itself more densely packed. The factors that influence density are much the same as the ones that were discussed earlier to explain variations in sound velocity. There are, of course, some exceptions; cyclohexane is denser than n-dodecane but dodecane facilitates faster propagation of sound waves. Similar observations can be made between isooctane and n-heptane, respectively. These types exceptions are expected because sound velocity is a function of both compressibility and density, and although these two parameters are determined by similar factors, they are not perfectly correlated.

To further investigate the previously mentioned exceptions, the relative strength of the dispersion forces in each of the hydrocarbons must be considered. To do this, isentropic compressibility was calculated via Equation 26 and plotted against temperature in Figure 24. It was found that within the scope of this investigation, liquids with higher compressibilities exhibit lower acoustic velocity. So clearly the exceptions highlighted earlier apply when comparing the compressibilities and densities of liquids as well. It was previously stated that density and compressibility are related, but not necessarily perfectly correlated. This is because they are dependent of related parameters, such as molecular spacing.

Density is primarily determined by the closeness of equilibrium packing of molecules under given conditions, the closer molecules pack together, the more dense the liquid. While compressibility is determined by intermolecular forces (in this case dispersion forces), which increase as molecular
spacing decreases. So effectively as density increases, compressibility should decrease. However, this rule breaks down when comparing cyclohexane to n-dodecane and n-heptane to isooctane. This is because intermolecular forces are also largely dependent upon molecular size. A long chained hydrocarbon like n-dodecane is conducive to large momentary dipoles making dispersion forces stronger than those found in cyclohexane, despite cyclohexane’s relatively large surface area. However, n-dodecane’s longer carbon chain does not affect density enough to overcome the packing capabilities of cyclohexane. In this case molecular shape has a greater affect on density than carbon number, while carbon number affects dispersion forces more than molecular shape. In the case of n-heptane and isooctane it is observed that the liquid with the higher carbon number has a higher density, despite it’s branched structure. From this it can be deduced that the effect of branching on packing efficiency is negligible, as the 3 branched methyl groups did not hinder packing enough to compensate for the increased density from the additional carbon. Whereas in the previous example the cyclic structure was able to overcome the density effects of 6 additional carbons in the parent chain. This example also differs from the previous one, as the heavier molecule has a higher value of isentropic compressibility. This means that the effect of 3 branched methyl groups reduced the intermolecular forces enough to compensate for the additional carbon. The likely mechanism for this is the reduced electron cloud overlap due to the decreased surface area associated with the branched alkane.

These examples illustrate the complexity of the effects from molecular shape, size, and bonding on physical properties of hydrocarbons. They also provide preliminary data that could be useful for designing an experiment to test and quantify these effects in future research.
Figure 24: Isentropic compressibility of hydrocarbons as a function of temperature

Once again Equation 27 was used to model the compressibility data as a function of temperature, and the coefficient values for each liquid can be seen in the appendix.

\[ \kappa_s(T) = AT^2 + BT + C \]  

(27)

To further display the differences between n-alkanes and the other hydrocarbons under investigation, the data from Figure 18 was superimposed on the surface plot showing carbon number as a function of temperature and compressibility in n-alkanes.

Figure 25 shows clear separation by hydrocarbon class; the branched alkanes lie above the n-alkane plane, while the cyclic hydrocarbons lie beneath it. This shows promise as a means of characterizing a liquid mixture using ultrasonic techniques with the aid of an independent carbon number estimate, and warrants further investigation.
Figure 25: Carbon number of hydrocarbons as a function of temperature and compressibility

The temperature and isentropic compressibility dependent carbon number model for n-alkanes was used to values for each of the non-normal hydrocarbons. The resulting figures and their error as a percent of the true value are tabulated below in Table 4.

Table 4: Evaluation of calculated carbon number values in other hydrocarbons

<table>
<thead>
<tr>
<th>cycloHexane</th>
<th>isoHexane</th>
<th>isoOctane</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>Error</td>
<td>Value</td>
<td>Error</td>
</tr>
<tr>
<td>35 Celsius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.30</td>
<td>88.34%</td>
<td>5.37</td>
<td>10.51%</td>
</tr>
<tr>
<td>45 Celsius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.05</td>
<td>84.17%</td>
<td>5.40</td>
<td>9.97%</td>
</tr>
<tr>
<td>55 Celsius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.83</td>
<td>80.57%</td>
<td>5.42</td>
<td>9.60%</td>
</tr>
</tbody>
</table>

The calculated carbon numbers are erroneous in all 4 liquids, which was expected based on previous comparisons and the graphical representation in Figure 25. The n-alkane model is clearly...
unsuitable for predicting carbon number in other types of hydrocarbons. However, these large error margins could potentially be useful for detecting the presence of non-normal hydrocarbons, especially in those with the greatest deviation from the model. The highest amount of error is found in toluene, the second highest in cyclohexane, then iso-octane and isohexane, respectively. This order is logical as toluene’s structure differs the most from n-alkanes, and isohexane the least (having only 1 branched methyl group, where iso-octane has 3). It can also be observed from the table that as temperature increases, the error decreases. This may be coincidence, but it is also possible that as temperature increases the behaviour of hydrocarbons converge toward that of n-alkanes. A more detailed investigation of this behaviour is needed to gain further insight.

The relationship between density and acoustic velocity could potentially be useful for determining the dominant class of hydrocarbon in a mixture. Figure 26 shows the observed acoustic velocity of each hydrocarbon investigated as a function of its density at both 30 and 50°C. The n-alkanes and paraffinic mineral oil follow a distinct curve at any given temperature, while the other hydrocarbons lie below said curve. By observing Figure 26 one can also deduce that more drastic deviations from a linear molecular shape results in greater separation from the n-alkane curve. For example; iso-octane, having 3 branched methyl groups, is farther from the curve than isohexane, which has only 1 branched methyl group. By performing a more thorough investigation of the relationship between molecular shape and the velocity to density ratio, the dominating class of hydrocarbon in a mixture could potentially be determined based on its location on a graph of acoustic velocity as a function of density.
The relationship between isentropic compressibility and density can be used in the same manner as the acoustic velocity and density relationship. However, branched alkanes appear to deviate from the curve to a lesser degree in terms of compressibility, and as such would be less suited to differentiating between different types of alkanes (Figure 27).

Figure 27: Compressibility of hydrocarbons as a function of density at 30 and 50°C
Table 5 contains experimental and literature values for velocity, density and compressibility for each of the 4 liquids studied in the previous section. With the exception of isohexane (which will be discussed later), experimental and literature values agree exceptionally well (within 0.3%).

Table 5: Experimental and literature values of ultrasonic parameters for other hydrocarbons

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Acoustic Velocity (m/s)</th>
<th>Mass Density (kg/m³)</th>
<th>Compressibility (TPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Lit.</td>
<td>Exp.</td>
</tr>
<tr>
<td><strong>Cyclohexane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1226.9</td>
<td>1228 h</td>
<td>769.81</td>
</tr>
<tr>
<td>40</td>
<td>1178.1</td>
<td>1180.5 i</td>
<td>759.46</td>
</tr>
<tr>
<td>50</td>
<td>1130.4</td>
<td>1132.86 j</td>
<td>749.12</td>
</tr>
<tr>
<td>60</td>
<td>1083.7</td>
<td>1086.49 j</td>
<td>738.77</td>
</tr>
<tr>
<td><strong>IsoHexane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1032.8</td>
<td>1016.5 i</td>
<td>649.05</td>
</tr>
<tr>
<td>40</td>
<td>987.3</td>
<td>921.8 i</td>
<td>638.73</td>
</tr>
<tr>
<td>50</td>
<td>941.4</td>
<td>927.3 i</td>
<td>628.4</td>
</tr>
<tr>
<td><strong>IsoOctane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1061.0</td>
<td>1061.6 l</td>
<td>689.23</td>
</tr>
<tr>
<td>40</td>
<td>1019.4</td>
<td>1019.1 l</td>
<td>684.47</td>
</tr>
<tr>
<td>50</td>
<td>978.1</td>
<td>977.9 l</td>
<td>674.95</td>
</tr>
<tr>
<td>60</td>
<td>937.1</td>
<td>935.8 l</td>
<td>665.43</td>
</tr>
<tr>
<td><strong>Toluene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1281.1</td>
<td>1283.3 m</td>
<td>856.91</td>
</tr>
<tr>
<td>40</td>
<td>1238.5</td>
<td>1240.6 m</td>
<td>846.87</td>
</tr>
<tr>
<td>50</td>
<td>1195.5</td>
<td>1198.6 m</td>
<td>836.82</td>
</tr>
<tr>
<td>60</td>
<td>1155.8</td>
<td>1157.2 m</td>
<td>826.77</td>
</tr>
</tbody>
</table>

[h] (Oswal, et al., 2005) [i] (Gascon, et al., 2000) [j] (Cerdeirina, et al., 2001) [k] (Silva, et al., 2009) [l] (Plantier & Daridon, 2005) [m] (Luning Prak, et al., 2014)

In the case of isooctane, experimental velocity and compressibility values are nearly identical to those reported by Plantier & Daridon (2005), having mean errors of 0.06% and 0.08%, respectively. However, the density figures do show a slight discrepancy; having a mean error of 1.10%. Although this amount of error initially seemed strange, a closer look at the literature values revealed that they were estimates made using ultrasonic properties. With this information, this
amount of error was deemed acceptable. To further verify the validity of the experimental density measurements the temperature-dependent density curve for isoocatane (shown in Figure 23) was extended to 20°C and compared with the density reported on the certificate of analysis from the supplier. The specific gravity value extrapolated from the experimental data was ~0.695, which agrees with the range of 0.691 and 0.696 reported by the supplier.

3.6.3 Detection of impure sample – Test of technique

In the initial tests conducted with the n-hexane available from Western University’s chemistry stores, it was observed that measured values of acoustic velocity and compressibility were significantly different from those found in literature. As reported in Table 3, the measured values of acoustic velocity are within 0.5% of literature values and measured compressibilities are within 1% of literature values. For the apparent n-hexane sample used initially, measured velocity was on average ~1.24% above those found in literature, while compressibility values were about 4.38% below reported literature values. These discrepancies prompted an investigation into the purity of the n-hexane sample, which revealed that the liquid in question was only 60% n-hexane by volume. The remainder of the solution was made up of the other 4 isomers of C₆H₁₄ and methylcyclopentane.

Table 6: Comparing hexanes blend to literature values for n-hexane

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Acoustic Velocity (m/s)</th>
<th>Mass Density (kg/m³)</th>
<th>Compressibility (TPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Lit.</td>
<td>Exp.</td>
</tr>
<tr>
<td>Hexanes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1068.3</td>
<td>1056ᵃ</td>
<td>664.10</td>
</tr>
<tr>
<td>40</td>
<td>1022.5</td>
<td>1009.5ᵇ</td>
<td>654.03</td>
</tr>
<tr>
<td>50</td>
<td>977.49</td>
<td></td>
<td>643.95</td>
</tr>
<tr>
<td>60</td>
<td>932.48</td>
<td>920.7ᵇ</td>
<td>633.87</td>
</tr>
</tbody>
</table>

[a] (Oswal & Maisura, 2002)  [b] (Boelhouwer, 1967)  [c] (Alekerov, 1975)
Isohexane’s experimental data also deviated from literature values, with mean errors of 1.57%, 0.72% and 3.77% for acoustic velocity, density, and isentropic compressibility, respectively. Upon further investigation of the isohexane used in this study, a certificate of analysis revealed that up to 5% of its volume is made up of other isomers of hexane, including methylcyclopentane. Whereas the comparable literature values, prepared by Plantier & Daridon (2005), used 2-methylpentane that was in excess of 99% pure. Therefore, it is quite likely that differences in isohexane purity contributed to the disagreement between experimental and literature values.

3.6.4 Measurements in binary mixtures of hydrocarbons

In this section, mixtures of different alkanes with n-heptane were investigated over a range of volume fractions (corrected to 30°C) from 0 to 1, testing on intervals of approximately 10 vol%. Acoustic velocity measurements were collected using the same sampling techniques as the previous tests, and were plotted as a function of volume fraction of the selected liquid being added to n-heptane.

![Figure 28: Acoustic velocity as a function of volume fraction in n-heptane](image)
Following observations can be made from the results plotted in Figure 28:

- Measurements at $X \approx 0.1$ yielded changes in acoustic velocity between 3.4 and 19.8 m/s; both of which exceed the observed mean measurement error of $\pm 0.45$ m/s.
- Acoustic velocities increase linearly with the addition of higher n-alkanes i.e. n-nonane and dodecane.
- There is linear decrease in acoustic velocity with the addition of n-hexane due to addition of lower carbon number n-alkane.
- The measured acoustic velocities are the lowest in solutions of isoheptane in n-heptane. Thus branching of the straight chain would further lower the acoustic velocity.
- Acoustic velocities in the solution of isoctane (highly branched molecule) are lower than those in n-heptane and in fact are closer to n-hexane values. This again is a result of branching of the molecule which is expected to affect both density and compressibility. It is expected that n-octane solutions will lie above the reference line.
- The role of molecular structure is also clearly observed in the solutions of cyclohexane since the values are well above the reference line. The velocity curve is also more curved.

In Figure 28 linear correlations are used to model the effect of volume fraction on acoustic velocity in all but two cases - cyclohexane and isoheptane. However, a certain amount of variation from these models is expected, as a truly linear relationship would require that the presence of the one
liquid did not affect the properties of the other. In this case all properties of the mixture would be the exact weighted average of the properties of the individual liquids. Mixtures typically approach said conditions when its components exhibit similar traits (ideal mixture), as the molecular interactions will be closer to those of the pure liquids. It is for this reason that many of the liquids were adequately modelled by linear functions. Isohexane and cyclohexane, however, had a second order polynomial coefficient that was statistically significant at the 95% confidence level. This was not entirely surprising, as they each differ significantly from n-heptane in terms of shape and physical properties.

\[ V(X) = AX^2 + BX + C \]  \hspace{1cm} (32)

Figure 30: Isentropic compressibility as a function of volume fraction in n-heptane

Isentropic compressibility was calculated for each sample using Equation 26, as it was in previous sections. The difference with these tests being that density was calculated using the Peng-Robinson equation of state, instead of using experimentally determined values. This choice was made to
reduce the amount of time between tests, thus minimizing losses of volatile components and error in the concentrations of samples.

Compressibility was observed to vary quadratically in cyclohexane, isohexane and n-dodecane. However, in the case of n-hexane, isoctane, and n-nonane the first quadratic coefficient was found to be statistically insignificant. Therefore, models for compressibility behaviour in the latter 3 liquids were adequately modelled using linear equations. The general equation for isentropic compressibility as a function of volume fraction in n-heptane is shown below in Equation 33, and the corresponding coefficients for each liquid are tabulated in the appendix.

\[
\kappa_s(X) = AX^2 + BX + C
\]  

(33)

Although in the case of compressibility most correlations have statistically significant quadratic coefficients, behaviour approaches linearity in liquids that are more similar to n-heptane. Again, this is due to the fact that molecules with more similar molecular size and shape exhibit similar intermolecular forces and packing efficiency. Therefore, they will disrupt the current equilibria in intermolecular spacing and attractive forces less. However, it should not be overlooked that as the rate of change in measured quantity decreases, noise and some sources of error account for a greater fraction of the variation in the data. This could potentially inflate the standard error of the quadratic coefficient ‘A’.

3.6.4.1 Deviation from ideal binary mixture

Ideal behaviour assumes that properties of mixtures are the molar weighted averages of the properties of its components. This is why it is more common-place in academia to see the composition of mixtures represented in terms of mole fractions. To examine whether the mixtures in this section approached ideal behavior, each parameter was compared to its ideal counterpart:
Equation 34: Ideal acoustic velocity of a binary mixture

\[ v^{id}(x) = xv_a + (1 - x)v_b \]  

Where \( x \) is the mole fraction of component ‘a’

Ideal compressibility was calculated in the same manner and then both sets of data were used to compute excess quantities for each set of mixtures, which are simply the difference between the measured and ideal values.

Equation 35: Excess acoustic velocity of a binary mixture

\[ \Delta v(x) = v^{exp}(x) - v^{id}(x) \]  

Figure 31: Excess acoustic velocity as a function of mole fraction in n-heptane

Deviation from ideal velocity reaches a maximum at approximately \( x = 0.5 \), which is expected as the probability of two components of a binary mixture interacting is maximized in equal parts solutions. It is also evident that the alkanes that are more similar to the “continuous phase” (n-heptane) cause less deviation. The points belonging to n-hexane, n-nonane, and isoctane are all very close to \( \Delta v = 0 \) m/s, iso-hexane is slightly above and reaches a maximum deviation of about
5 m/s. Highest deviations are obtained with n-dodecane and cyclohexane approaching 20 and -20 m/s, respectively. It can only be said of cyclohexane that its mixing effects definitively act negatively on acoustic velocity. To be clear, the addition of cyclohexane increases the acoustic velocity in n-heptane but the effects are diminished by mixing. Thus n-heptane prevents cyclohexane from forming the lattice-like packing structure, which is largely responsible for its rigidity.

![Figure 32: Excess isentropic compressibility as a function of mole fraction in n-heptane](image)

Similar trends can be realized in the plot of excess compressibility; deviation is maximized at equal parts and the alkanes with similar properties to those of n-heptane approach ideal behaviour. However, in the case of compressibility the majority of the deviation is negative and the magnitude of n-dodecane’s deviation is approximately triple that of cyclohexane. Also, cyclohexane is the only entity wherein mixing effects compressibility positively. This is again due to the fact that the
unique properties of a cyclic molecule, in this case its increased surface area, are less apparent when they are not constantly interacting with like-molecules.

The temperature and compressibility dependent model for carbon number in n-alkanes (Equation 31) was evaluated as a means of estimating the average carbon number of a hydrocarbon mixture. The values calculated using Equation 31 were compared to weighted averages of the carbon number for each sample that was investigated, representing the absolute error between the two as a percentage of the weighted value. It was observed that generally in the mixtures containing only n-alkanes the model was reasonably accurate, with a range in error of 0.21 - 4.13%. It was observed in these mixtures that error typically reached a maximum around X = 0.5, then began to decline again. This is expected as the effects of mixing in a solution are greatest when at equal parts. In the other solutions the error behaviour was quite different; increasing constantly and eventually reaching a maximum at X = 1. Again, this was anticipated as it was revealed in 3.6.2 that Equation 31 fails for cyclo- and isoalkanes. The range of error for these mixtures was 0.36 – 78.17%. The data from these comparisons is tabulated in Table 7 below.

Table 7: Evaluation of calculated carbon numbers in binary mixtures

<table>
<thead>
<tr>
<th>X (approx.)</th>
<th>Value</th>
<th>Error</th>
<th>Value</th>
<th>Error</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-Hexane</td>
<td>cycloHexane</td>
<td>isoHexane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.123</td>
<td>1.76%</td>
<td>7.123</td>
<td>1.76%</td>
<td>7.123</td>
<td>1.76%</td>
</tr>
<tr>
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</table>

It should be pointed out that the values for volume fraction in the table are approximate, but the weighted values in the Table 7 were calculated using the actual volume fractions at 30°C.

3.6.5 Observations in complex mixtures of hydrocarbons

After studying the ultrasonic parameters of binary hydrocarbon mixtures, the scope of the investigation was expanded to include mineral oil, a blend of long chain and largely paraffinic hydrocarbons. Response in ultrasonic parameters to variations in temperature were tested using similar protocol to sections 3.6.1 and 3.6.2. Acoustic velocity and isentropic compressibility of mineral oil exhibit similar behaviour as the pure hydrocarbons, with respect to changes in temperature. However, the values were drastically different. Mineral oil facilitated much higher acoustic velocities and has much lower values of isentropic compressibility. This is due to the long hydrocarbon chains that compose mineral oil, as well as the likely presence of cyclic alkanes.
The observed higher acoustic velocity and lower compressibility are consistent with the general trend observed in pure hydrocarbons; as chain length increases velocity increases and compressibility decreases. To convey the magnitude of the differences in ultrasonic parameters, between mineral oil and n-alkanes the models developed for n-dodecane (the n-alkane with values closest to those of mineral oil) were superimposed on the mineral oil data in Figure 33.

To investigate the effects of varying concentrations in a complex mixture, n-heptane was systematically added to mineral oil in increments of ~10% by volume, corrected to 30°C. Each of the 11 samples were tested in the same manner as the binary mixtures discussed earlier. However, in this case the data was plotted as a function of heptane content in mineral oil. That is to say that at $x = 0$ the sample is 100% mineral oil, whereas in the previous experiments $x = 0$ denoted a sample that was 100% n-heptane. Another difference between this set of experiments and the binary mixtures runs is how density was calculated. Since Peng-Robinson coefficients were
unavailable for this specific blend of mineral oil, the density values were estimated as the volume fraction weighted average of the density of mineral oil and n-heptane at 30°C.

![Graph showing acoustic velocity and isentropic compressibility as a function of n-heptane content in mineral oil](image)

**Figure 34:** Velocity and compressibility as a function of n-heptane content in mineral oil

Acoustic velocity decreased with each addition of heptane, while isentropic compressibility increased. These trends agree with those observed in binary mixtures, where the addition of lighter ends (n-hexane, isohexane, & isoctane) resulted in similar changes in the ultrasonic parameters. However, it should be pointed out that the rate of change in acoustic velocity with respect to heptane content in mineral oil is variable whereas in the binary mixtures it remained constant (in most cases). This is likely due to the diversity of the compounds present in the mineral oil, which contains hydrocarbons of various sizes and shapes. In practical applications it is unlikely that a specific entity will be monitored over a range of 0-100%, it is more likely to be tracked within a region of interest, for example 0-15% by volume. This is important to point out because over short ranges the rates of change in both velocity and compressibility can be assumed to be constant, and as such a complex mixture like heptane enriched mineral oil can be treated as a binary mixture.
\[ V(X) = 463.87X^3 - 737.04X^2 - 19.070X + 1407.9 \quad (36) \]

\[ \kappa_s(X) = 327.16X^2 + 305.31X + 578.16 \quad (37) \]

3.6.5.1 Loss of volatile monitoring in complex mixtures

It was decided to investigate complex mixture monitoring as a viable option for detecting light-end losses from heavier fractions. Initial tests with crude oil showed that at a given temperature, the measured acoustic velocity changed with time. This was attributed to the presence (and loss) of volatile components (C6 and lighter) in crude oil.

Figure 35: Acoustic velocity in crude oil as a function of time

Figure 35 compares variations of acoustic velocity with time in fresh crude at 30 and 60°C respectively. It can be seen from the figures that there is a gradual increase in acoustic velocity over time. As expected, the rate of change is higher at 60°C compared to 30°C. These results suggest that ultrasonic monitoring can be used to detect volatile losses from heavier mixtures.
The effects of volatile losses from crude oil were investigated by comparing fresh crude oil samples (from sealed container) with stabilized crude oil. Fresh crude oil sample was stabilized by heating the sample to about 60 °C in open container and maintaining the temperature for nearly 24 hours with gentle agitation. The crude oil sample was cooled back to ambient temperature before the experiment.

The next set of experiments investigated the effects of adding/removing lighter component n-hexane from heavier mineral oil and stabilized crude oil samples. N-hexane was selected to represent the volatile fraction in crude oil. Hexane was added in 2 vol% increments up to 10 vol% (corrected to 30°C), and was tested after each addition. This process was then repeated with both mineral oil and crude oil. The resulting velocity data from each trial was plotted as a function of hexane content and can be seen below in Figure 36.

Figure 36: Acoustic velocity in hydrocarbon blends as a function of hexane content
The stabilized crude and mineral oil exhibited very similar acoustic velocities before hexane is added. It can also be observed that hexane additions cause the speed of sound in each fluid to decrease linearly. However, there is an important difference that should be noted; as hexane was added the velocity values began to diverge significantly. The rate of change in acoustic velocity, with respect to hexane content, was larger in crude oil than in mineral oil. The observed difference in rate of change could be explained by similarities, or differences, between the structure of n-hexane and the oil mixture to which it is added.

Mineral oil is a mixture of mostly paraffinic hydrocarbons in the carbon number range of 14 to 30, crude oil is far more complex mixture consisting of all types of hydrocarbons and a much wider range of carbon number. As previously stated, the intermolecular forces in a fluid are governed by the molecular structure of its components. So the molecular arrangement and overall strength of intermolecular forces in a liquid should be disrupted less significantly by the addition of compounds with similar structure, than if a dissimilar compound was added. Mineral oil largely consists of paraffinic hydrocarbons which have similar structures to that of n-hexane. Whereas crude oil is composed of many different classes of hydrocarbons and other contaminants. Some of these include asphaltenes, aromatics, branched alkanes etc. This suggests that the effect of hexane on average strength of intermolecular forces, and thus the acoustic velocity, should be greater in crude oil than in mineral oil.

A number of multicomponent mixtures, in practice, contain small amounts of volatile components that can be lost via evaporation. These seemingly negligible losses can become significant over time and can be quite costly from both financial and environmental perspectives. For these sets of experiments hexane rich samples of crude oil and mineral oils were used to record changes in acoustic velocity with time when subjected to constant temperature and agitation. Samples were
tested every hour for 10 hours and maintained at 30°C and comparisons were also made with fresh crude, stabilized crude and mineral oil. The results presented in Figure 37 clearly show gradual increase in acoustic velocity in n-hexane enriched crude oil, mineral oil and fresh crude, which is consistent with previous observations - as lighter ends are lost, the speed of sound increases.

Figure 37: Acoustic velocity in hydrocarbon blends as a function of time (30°C)

Changes in acoustic velocity were significant after the first measurement, the smallest change of 2.61 m/s being realized in crude oil at 30°C. Although this is seemingly insignificant, it exceeds the observed measurement error of ±0.48 m/s. It should also be noted that velocities in mineral oil and stabilized crude remain essentially constant. This is to be expected, as neither contain compounds that are volatile at 30°C.
3.6.6 Signal attenuation measurements

The second parameter that was directly measured using the ultrasound equipment is the signal strength, or amplitude. As shown in Figure 38, the amplitude of the transmitted signal is affected by the type of the medium and its temperature. It is observed that transmitted signal strength increases with an increase in carbon number in n-alkanes and decreases as temperature is increased. Thus the lowest amplitude of a transmitted signal is obtained with n-hexane and the highest with n-dodecane.

![Figure 38 Signal amplitude in n-alkanes as a function of temperature](image)

It should be however, pointed out that the absolute value of amplitude is subject to the influence of many factors including equipment wear, fouling, and even minor variations in the power supply parameters. This can be minimized to a large extent by calculating signal attenuation using Equation 23 which uses a reference amplitude that is measured simultaneously. The reference amplitude can be the initial value (before transmission) or it can be received amplitude of a reference sample.
\[ \alpha = \frac{1}{d} \ln \left[ \frac{A_{\text{ref}}}{A} \right] \]  

In this study n-hexane was selected as the reference or stock solution for the calculation of attenuation coefficients. By using this approach, the values obtained through these experiments will be relative values of attenuation. That is to say that they are relative to the attenuation that would be realized by the wave if it were propagating through n-hexane, with all other parameters being equal. These relative values of attenuation are plotted as a function of temperature in Figure 39 for the n-alkanes.

![Figure 39 Attenuation coefficient in n-alkanes as a Function of temperature](image)

The negative attenuations obtained are a result of selecting n-hexane as the reference used in this study. It is also evident that the attenuation coefficient becomes more negative as temperature increases. Initially one may assume that this indicates less wave attenuation as temperature
increases, however that is not the case. The shape of said curves simply indicates that the rate of change in wave attenuation with respect to temperature is greater in n-hexane than the other n-alkanes under investigation.

Signal amplitudes obtained in other hydrocarbons are plotted in Figure 40 as a function of temperature. It is observed that signal amplitudes in isohexane are significantly lower than those observed in n-hexane, while cyclohexane produced a much stronger signal. This suggests that with further investigation amplitude and attenuation may be used to detect the presence of branched or cyclic compounds in an otherwise paraffinic liquid.

The effect of adding n-heptane (a lighter fraction) to mineral oil on signal amplitude was also investigated for a potential application. As expected, signal amplitude decreased with increasing fraction of n-heptane in solution, while corresponding attenuation coefficients increased (Figure 41).
Attenuation coefficient undergoes almost exponential growth as heptane is added. Thus high sensitivity of the technique can be used to track lighter components in heavier mineral oil fraction. These observations can be combined with velocity measurements to improve the accuracy of the technique.

3.7 Conclusions

The potential of ultrasonic techniques for use in monitoring composition changes in hydrocarbon liquids is demonstrated using the results of the previous systematic testing. Ultrasonic wave parameters, such as acoustic velocity and attenuation coefficient, are largely dependent upon the characteristics of the media though which the waves propagate. These parameters are useful for drawing conclusions about the nature of the media under investigation. By studying ultrasonic responses to different stimuli, including temperature, composition, and molecular size and
structure, one can begin to understand how each of these effects the aforementioned ultrasonic parameters as well as some thermodynamic quantities, such as compressibility and acoustic impedance. These relationships can then be exploited to develop a system wherein an organic liquid can be characterized in terms of carbon chain length and hydrocarbon class using experimental ultrasonic parameters.

Compressibility correlations with temperature and carbon number in n-alkanes were used to develop an equation that could predict the carbon number of pure and mixed n-alkanes based on compressibility and temperature. Carbon number in pure n-alkanes could be predicted within 4% error, and within 4.13% error in binary mixtures of n-alkanes. The correlation was also able to provide a reasonable estimate of the average carbon number of a mineral oil, 19.75 compared to a GC/MS estimation of 21-22.

Extensive testing of the technique in binary mixtures demonstrated its viability for monitoring targeted components in product streams for quality control purposes. The concentration changes of the selected component in the stream can be monitored via tracking acoustic velocity. This was demonstrated by using ultrasonic parameters to determine that the quality of n-hexane sample supplied to the lab was not pure. The real world application would include a minimum of two ultrasonic sensors; one in the fluid under observation and the other in a stock solution for comparison. By doing this, sampling error can be mitigated and relative changes can be tracked to provide additional information about the liquid. The second application highlighted in this paper is the use of ultrasonics for detecting the loss of valuable light ends via evaporation. This can be done by tracking changes in ultrasonic parameters over time. The concept was proven plausible by showing the drastic changes in acoustic velocity (~32 m/s) after allowing a crude oil sample to sit in a fume hood in an open container for 24 hours.
3.8 Recommendations

The most important recommendation for future research is to widen the scope of the materials investigated. This paper serves as a proof of concept, but to obtain relationships that can draw more accurate conclusions about liquid mixtures there must be a more concrete understanding of how each physical characteristic affects ultrasonic parameters. It is suggested that the range and number of alkanes is increased and that the effects of structural differences are on ultrasonic parameters are more thoroughly investigated. By increasing the number of components investigated the degrees of freedom will also increase, which will decrease standard error and yield more accurate correlations.

This study effectively shows the basic differences in ultrasonic behaviour between linear, branched, and cyclic alkanes. Unfortunately with the available data these effects can not be accurately quantified. A systematic investigation of brached alkanes including the number of branched groups, their positions, and size via a full factorial experimental design could provide clearer picture of their effects.

In addition to expanding the scope of materials investigated, the conditions should be expanded as well. Tests should be done at higher temperatures and pressures to more accurately reflect industrial situations. There was an observed decrease in the error of estimated carbon number as temperature increased. It is possible that behaviour converges to that of alkanes as temperature increases. By performing experiments at higher temperatures this could be investigated.

Another major area that could be improved upon is the investigation of attenuation. With the current method of testing there are too many degrees of freedom to determine the absolute attenuation, and therefore values can’t readily be compared to literature or values computed via Stoke’s law. A possible way to reduce the amount of degrees of freedom is to modify the probe to
have two receivers with different path lengths that receive a signal from the same transmitter. The result will produce two different amplitude readings for the same signal over two different lengths, thus reducing degrees of freedom by one. Absolute attenuation could thus be solved and compared to other values and investigated more effectively.
3.9 References


Plantier, F., & Daridon, J. (2005). Speed of Sound of 2-Methylpentane, 2,3-Dimethylpentane, and 2,2,4-Trimethylpentane from (293.15 to 373.15) K and up to 150 MPa. *Journal of Chemical and Engineering Data, 50*(6), 2077-2081.


Urick, R.J., (1947), A sound velocity method for determining the compressibility of finely divided substance. *Journal of applied physics, 18*, 983-987
Chapter 4: Development of ultrasonic techniques for characterization of polar liquids

4.1 Introduction

A need was identified for online testing and characterization of polar compounds, mainly alcohols due to their growing commercial applications as renewable fuels. Alternative fuel sources, especially renewables are becoming increasingly popular as society becomes more concerned with environmental stewardship. Perhaps one of the most significant advancements in this field is the implementation of bio-alcohols as alternatives to fossil fuel based products. Modern day vehicles are all capable of using ethanol-blended gasoline, some of which can use fuels that are up to 85% ethanol by volume. Bio-butanol is another bio-alcohol which is expected to enter the biofuels market on a large scale. With the use of bio-alcohols becoming more widespread, the pursuit of producing fuel grade product while minimizing cost has become a common research topic. As a result, many new technologies and innovations to existing processes are being developed, creating a market for cost-effective and reliable process monitoring equipment.

Water is a major contaminant in ethanol production, and is difficult to remove beyond its azeotrope at approximately 95% ethanol. This is problematic because in order for ethanol to be suitable for blending with gasoline, it must be completely anhydrous. Therefore, it is crucial that ethanol product streams, especially those of emerging technologies, are monitored closely for water contamination. Current techniques for determining water content in ethanol include density tests, near-infrared spectral method, Karl Fischer titration and several others. These tests can provide excellent accuracy, however they are difficult to automate and require regular maintenance and calibration.
4.2 Project outline and objectives

Ultrasonic technology has shown potential for online monitoring of organic liquids. Chapter 3 discusses in detail its suitability for characterizing liquid hydrocarbon mixtures. This chapter aims to apply similar techniques and methodology to develop procedures and correlations that will aid in monitoring liquid mixtures that contain liquids such as alcohols and water. The objective is to devise a system wherein ultrasonic parameters can be used to characterize mixtures containing such liquids.

Initial stages of research will include studying the behaviour of ultrasonic parameters in water and alcohols at different concentration levels. Each liquid’s physical characteristics will then be used to account for any unique trends observed in acoustic velocity, isentropic compressibility, or acoustic impedance. Observed correlations will then be used as a means of making conclusions about unknown polar liquids using experimental ultrasonic parameters. Lastly, an algorithm implementing said correlations will be designed, along with a proposed schematic of the apparatus necessary for each specific application discussed.

4.3 Basic theory

Consider two transducers; a transmitter and a receiver, both submerged in a liquid medium and separated by a fixed distance, \( d \). If an ultrasonic wave is produced at the transmitter and subsequently detected by the receiver, the time it takes for the signal to be picked up is known as the time-of-flight (TOF). The distance between the transducer and the receiver, along with the TOF can then be used in Equation 38 to calculate the speed of sound in the given medium.

\[
v = \frac{d}{\text{TOF}} \quad (38)
\]
Sound propagates through media as compression waves. This is accomplished via alternating compression and rarefaction of the media in question. Since displacement caused by the passage of the acoustic waves is infinitesimally small, it can be safely assumed to be harmonic in nature. Equations based on this concept, such as the Newton-Laplace equation, present acoustic velocity as a function of the isentropic (or adiabatic) compressibility and density of the medium through which sound is propagating. This relationship can be seen Equation 39 (Ament, 1953; Urick, 1947).

\[
v = \frac{1}{\sqrt{\kappa \rho}}
\]  

By rearranging Equation 39, experimental values for acoustic velocity and density can be used to determine the isentropic compressibility of a given fluid. Compressibility refers to a fluid's ability to compress thereby reducing its specific volume when subjected to an external force. Isentropic compressibility specifically refers to the ratio of volume change to external pressure when entropy is held constant. By determining compressibility, a better understanding of the driving forces behind ultrasonic interactions can be achieved.

Another parameter that can readily be calculated using velocity and density is acoustic impedance, which quantifies the amount of resistance a medium has toward the acoustic pressure that facilitates the propagation of sound waves (Kinsler et al., 2000).

\[
Z = v \rho
\]

In order to use these two parameters to draw conclusions about a medium with confidence, responses to varying conditions must be investigated thoroughly. In this experiment variations in acoustic velocity will be tested for correlations with changes in temperature and media
composition. Understanding how these parameters behave in response to different types of media manipulation will provide information that will allow for characterization of more complex mixtures.

4.4 Experimental apparatus

Ultrasonic wave parameters are to be tested over a range of temperatures and through different media, of varying compositions. The vessel used to contain the medium under observation is a 1800mL jacketed glass tank. According to Adamowski et al. (1995) ultrasonic measurements of acoustic velocity are not affected by flow rate, providing that cavitation does not occur. This means that the stationary model used in this experiment can adequately represent an industrial setting.

To regulate the temperature of the media, a PolyScience temperature controller, also known as a water box, feeds water into the jacket of the vessel. To maintain a uniform temperature profile throughout the medium, a vertical agitator stirs the contents of the tank. Fixed to the vessel is a type K thermocouple, which is used to monitor the temperature of the fluid. A detailed schematic of this set up can be seen below in Figure 42.

Figure 42: Schematic of experimental set-up
A probe specifically designed for this project is supported by a fixed stand, which allows it to be partially submerged in the liquid. The probe is equipped with two transducers, a 3.5MHz ultrasonic wave transmitter and a receiver fixed with ~5 cm of separation between them. A detailed scale diagram of the probe can be seen in Figure 43.

![Diagram of transmitter-receiver probe](image)

**Figure 43**: Diagram of transmitter-receiver probe

The probe was connected to a UT340 pulse receiver by UTEX Scientific Instruments Inc. The pulse receiver sent signals to the transducer to produce an ultrasonic wave train, generating a pulse at a rate of 20kHz, or every 50\(\mu\)s. The unit was also responsible for receiving the ultrasonic signals from the receiver transducer. Received signals were plotted on a plot of voltage vs. time using software called InspectionWare 64. From this signal peaks provided time of flight and amplitude data. Peaks had a width of <2ns, which for reference, is approximately 0.0057% of a 35\(\mu\)s time-of-flight. This equipment can be seen as a part of the set up in Figure 42, while an example of the signal produced by the wave can be seen in Figure 44.
The strength of the received signal can be determined by the height of the peak in relation to the Y-axis, which has units of volts. This information is important when studying the implications of the attenuation coefficient through a specific medium. The time-of-flight of a signal is the time it takes the ultrasonic wave to move from the transmitter to the receiver. This can be determined by inspecting where the major signal peak shows up in relation to the X-axis, which is in units of microseconds. The fact that the transmitter and receiver are a fixed provides a constant path length and ensures good alignment. Both of which make calculating experimental acoustic velocity very simple, using Equation 38.

The density of each pure sample was tested using an Eagle Eye SG-Ultra Max Digital Hydrometer/Density Meter. Determining values for mass density allows for calculation of isentropic compressibility, and for correlations to be made with ultrasonic wave parameters. This will aid in enabling distinction between media of different compositions. A picture of the Density meter can be seen in Figure 45.
4.5 Materials and methods

The liquids under observation include 5 different alcohols, deionized water, and tap water. The alcohols include methanol, ethanol, 1- and 2-propanol, 1-butanol, and an azeotropic ethanol-water mixture (~95% ethanol).

Sampling techniques for the investigation are to be uniform throughout the entire experiment; Data is collected over 10 seconds at a sampling frequency of 100Hz, yielding 1000 time-of-flight values per run. The arithmetic average of each set of values is then calculated and subsequently used to compute acoustic velocity. The standard deviation of each will be calculated and used to ensure the data does not contain any extreme outliers.

Initial tests will be done in water over a temperature range of 25-60°C. Both deionized and regular tap are to be used to contrast the differences in their properties and to demonstrate the sensitivity of the ultrasonic method. Subsequently, salt will be added to water in linear increments of weight.
percent, until a 2% solution is achieved. Each solution will be examined at 30 and 60°C to investigate the effects that salinity have on ultrasonic parameters. Each test will be repeated twice, to yield 3 independent sets of data in an attempt to eliminate sampling error. By performing the experiments in tap water on different days, the likelihood of using an anomalous water sample is also reduced.

The next set of tests will be in alcohols, which will be examined over the same temperature range as the water samples. Next, binary mixtures of methanol, 1-propanol, 1-butanol, and deionized water in ethanol will be prepared and tested over a range of 0-20% by volume at 30°C. Samples in alcohols and alcohol based mixtures will only be performed once to limit exposure to the probe, as the protective epoxy coating is soluble in alcohols.

For the purposes of demonstrating a potential practical application wherein ultrasonic parameters can be used to determine the ethanol content in gasoline, n-heptane is used as an analogue for gasoline.

Table 8: Materials

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<td>N/A</td>
<td>From Tap</td>
</tr>
<tr>
<td>Sodium Chloride (Table Salt)</td>
<td>Windsor</td>
<td>99.99%</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>Alfa Aesar</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>
4.6 Results and discussion

4.6.1 Measurements in water

The initial set of tests were conducted in water, and investigated the effects of temperature on acoustic parameters over a range of 25-60°C. Figure 46 shows that as temperature increases, so does acoustic velocity. This behaviour differs from those observed in the organic liquids from chapter 3, in that the rate of change in velocity with respect to temperature is positive and decreases as temperature increases.

![Figure 46: Acoustic velocity of tap water as a function of temperature](image)

After conducting 3 sets of tests in tap water identical experiments were performed in deionized (DI) water. The results from the runs in DI water yielded similar trends and values, however the data was more consistent; The average deviation between minimum and maximum values in DI water was 0.085%, compared to 0.324% in tap water. The increased variability in the tap water experiments is likely due to fluctuations in dissolved components from day-to-day.
In both cases (tap and DI water) the relationship between temperature and acoustic velocity was modelled using a second degree polynomial. This relationship can be seen in Equation 41, and the specific coefficients for each liquid can be found in the appendix.

\[ v(T) = AT^2 + BT + C \]  \hspace{1cm} (41)

In chapter 3 the reason for velocity’s negative correlation with temperature was explained by the weakening of intermolecular forces. In the case of water, the observed correlation is opposite. This is because the intermolecular forces in water are more abundant (and much stronger) than those found in normal alkanes, and therefore require more external energy to be overcome. However, once temperatures are high enough to overcome said forces it must be the case that velocity will begin to decrease as temperature increases, as in most other liquids. This assertion is supported by the decaying rate of change in velocity observed in Figure 46 and Figure 47.
\[ \kappa_s = \frac{1}{V^2 \rho} \]  

(42)

Further explanation of this anomalous behaviour requires that the compressibility of water be examined over the same temperature range. To do this, the Newton-Laplace equation has been rearranged to solve for isentropic compressibility via density and acoustic velocity and the resulting data has been plotted as a function of temperature.

![Graph showing isentropic compressibility of DI water as a function of temperature.](image)

Figure 48: Isentropic compressibility of DI water as a function of temperature

\[ v(T) = AT^2 + BT + C \]  

(43)

From Figure 48 it can be observed that compressibility is decreasing as temperature increases until it reaches a minimum value of compressibility somewhere between 40 and 60°C. The polynomial curve suggests the minimum is located at \( \sim 53°C \), but without further runs this cannot be verified. The existence of the minimum is interesting because in most other fluids compressibility increases with temperature indefinitely, as spacing and kinetic energy of the molecules provides an environment more conducive to compression. However, the hydrogen bonding present in water
allows it to form large lattice-like structures known as icosahedral water clusters (Loboda & Goncharuk, 2010). As the hydrogen bonding network is deteriorated by the increased kinetic energy, the cluster begins to “pucker” or partially collapse in on itself. The overall structure becomes less ordered and as a result, previously non-bonded molecules are situated more closely. This effectively increases the amount of nearest neighbors each molecule has and therefore increases the structure has less available space to be compressed into itself. At a critical temperature the hydrogen bonding network will have completely collapsed, and the relationship between compressibility and temperature become more typical, which accounts for the parabolic shape observed in Figure 48. Mallamace et al. (2012) report this temperature to be 43 ± 5°C, which is within reason of the minimum observed from the experimental data.

Diagrams of the aforementioned cluster before and after the hydrogen bonding network begins to collapse can be seen below in Figure 49.

![Diagram of water cluster before and after puckering](image)

Figure 49: Water cluster before and after puckering (Chaplin, 2015)

Water’s anomalous behaviour is also observed in acoustic impedance, which increases with temperature until it reaches a maximum value somewhere between 40 and 60°C. This is expected
as impedance is closely linked to compressibility. A more compressible fluid is more conducive to deformation and therefore supplies less resistance to the compression waves that propagate sound. The experimental data suggests that the point at which impedance reaches a maximum is around 48°C, as depicted in Figure 50. However, the curve is only an approximation of the behaviour, so to definitively say where this point is, one would have to perform additional tests within the range of 40-60°C. It is likely that addition investigation would reveal similar local extreme values for impedance and compressibility.

![Figure 50: Acoustic impedance of DI water as a function of temperature](image)

\[ v(T) = AT^2 + BT + C \]  \hspace{1cm} (44)

The next set of experiments were performed in salt water (prepared from DI water and table salt) and tested over a range of salinity from 0-2% by mass. Tests were conducted at both 30 and 60°C to contrast the effects of salinity and temperature. The resulting sets of data were separated into two groups (based on temperature) and plotted as a function of salinity.
It was observed that acoustic velocity increased linearly as a function of salinity at both temperatures. However, at the 95% confidence level the rate of change with respect to salinity was statistically larger at 30°C; 10.588 ± 0.393 ms⁻¹wt%⁻¹ compared to 8.940 ± 0.486 ms⁻¹wt%⁻¹ at 60°C. This implies that as temperature increases, the effect that salinity has on acoustic velocity is less pronounced.

Another interesting observation regarding the rate of change in velocity is its sign; Since the addition of salt is known to increase the density of water, salinity’s positive effect on velocity implies that it must be negatively correlated with compressibility. This again can be accounted for by considering the hydrogen bonding exhibited by water. The clusters formed by hydrogen bonding depend on the attraction between positively charged hydrogen and negatively charged oxygen. So as salt is added, its respective dissociated ions impede hydrogen bonding by interacting with water’s dipoles. These interactions favour the compressed structure of the icosahedral clusters.
and thus cause compressibility to decrease via similar mechanisms as temperature does before reaching the aforementioned critical temperature.

![Figure 52: Isentropic compressibility of water as a function of salinity](image)

As was the case with velocity, the rate of change of compressibility with respect to salinity is of greater magnitude at 30°C than at 60°C. These observations support the rationale that was used to explain the overall sign of the relationships with salinity; As temperature increases hydrogen bonding is reduced, thereby limiting the effect that free floating ions can have on compressibility. This suggests that if salinity and temperature are sufficiently high, there could potentially exist a point at which further increases of salinity cause a reduction in acoustic velocity. This assumes that density continues to increase with salinity and that the point exists before saturation or phase change occur.

Acoustic impedance was also observed to have a linear correlation with salinity, and again the magnitude of the rate of change was greater at the lower temperature. This implies that saline solutions exhibit greater resistance to compression waves as salinity increases. This relationship
was anticipated as impedance will always increase as compressibility decreases. Linear coefficients for the salinity-dependent models of the acoustic parameter discussed can be found in the appendix. The general equation for each is as follows:

\[ v, \kappa, Z(S) = AS + B \]  \hspace{1cm} (45)

![Acoustic impedance of water as a function of salinity](image)

Figure 53: Acoustic impedance of water as a function of salinity

Although separating the data by temperature provides interesting visualizations of the effects salinity has on acoustic parameters, the data is not useful for practical applications when presented in such a way. A more useful way of representing the data is by fitting velocity (or either of the other two parameters) as a function of both salinity and temperature. This way both temperature and salinity can be treated as continuous variables and the correlation can be used to analyze any saline solution with parameters that fall within the salinity and temperature ranges.

\[ v(T, S) = -0.03262T^2 + 3.965T - 0.055S + 12.24S + 1422 \]  \hspace{1cm} (46)
The above equation was generated using the available experimental data, however it should be noted that the data is incomplete since solutions with salinity above 0wt% were only done at 30 and 60°C. By repeating the tests in salt water at various temperatures a more complete picture of the how one parameter effects the rate of change with respect to the other can be obtained, resulting in a more accurate model. From such a model salinity of a brine solution could be estimated using experimental values of temperature and acoustic velocity.

\[
S(T, v) = \frac{v - 1422 + T(0.03262T - 3.965)}{-0.055T + 12.24}
\]

(47)

Figure 54: Acoustic velocity in water as a function of salinity and temperature

4.6.2 Measurements in alcohols

The next set of experiments were performed in primary alcohols with carbon chain lengths ranging from 1-4 atoms long. The tests were conducted in a similar fashion as those done in water, with temperature ranging from 25-60°C. However, the runs in alcohol were only done once to limit the probe’s exposure, as its protective epoxy coating is soluble in high concentrations of alcohol.
First the effects of chain length on acoustic velocity were investigated and it was observed that acoustic velocity increased with chain length. This is consistent with the observations made in chapter 3; where longer alkanes exhibited faster ultrasonic velocities. In both cases this phenomenon is due to the larger increased capacity of molecules to facilitate temporary dipoles. Larger dipoles cause stronger dispersion forces, which create a more rigid fluid that is more conducive to rapid translation of compression waves.

![Graph showing acoustic velocity in primary alcohols as a function of carbon number](image)

Figure 55: Acoustic velocity in primary alcohols as a function of carbon number

\[ v(C) = AC + B \] (48)

However, the presence of a hydroxyl group in the structure of an alcohol facilitates other kinds of intermolecular forces, namely dipole-dipole interactions and hydrogen bonding. Both of these forces are the result of oxygen’s electronegativity causing it to draw electron density toward itself. In doing this both the terminal carbon on the opposite end of the molecule and the hydroxyl hydrogen assume a slight positive charge. Dipole-dipole interactions describe the attraction between the slightly-positive terminal carbon atom and the oxygen atom of neighboring molecules,
while hydrogen bonds describe the interactions between the positive hydroxyl hydrogen and neighboring oxygen atom. Both of these forces are much stronger than dispersion forces, and are the reason why short chain alcohols like methanol and ethanol are liquid at SATP, while their alkane analogues are gaseous.

Figure 56: Acoustic velocity in primary alcohols as a function of temperature

\[ v(T) = AC + B \] (49)

Next, the acoustic velocity in primary alcohols was plotted as a function of temperature. Again, the behaviour was observed to be similar to that of n-alkanes. As temperature increased the acoustic velocity decreased linearly. This observation indicates that despite the stronger intermolecular forces present in alcohols, compressibility is a function of temperature. If compressibility was a constant parameter the reduced density associated with heating would cause an increase in velocity, according to the Newton-Laplace equation. To calculate compressibility, density measurements were taken over a range of temperatures to create a profile for each alcohol.
It can be observed in Figure 9 that as temperature increases, each alcohol becomes less dense. It is also evident that generally, larger molecules result in more dense liquids. The exception to this trend is methanol. Over the investigated temperature range ethanol and methanol have very similar densities, despite methanol being a much smaller molecule. Methanol owes its increased density to its strong hydrogen bonding. Due to its short carbon chain, methanol's intermolecular interactions are dominated by hydrogen bonding, which causes it to behave somewhat anomalously. However, the methyl group limits oxygen to accepting only a single hydrogen bond, whereas in water each oxygen can make two bonds. Despite this, methanol still tends to form one-dimensional structures, held together by hydrogen bonds (Torrie et al., 1989). These tightly packed structures are conducive to close packing and facilitate its increased density.

Isentropic compressibility was calculated for each alcohol using the Newton-Laplace equation, and plotted as a function of temperature. Over the temperature range of interest compressibility
increased parabolically, indicating that as temperature increased so did its effect on compressibility. The positive correlation is caused by the increased kinetic energy of the liquid; molecules move faster and become on average further apart. The increased space between molecules and reduced intermolecular forces make the liquid more conducive to compression. The isentropic compressibility of each alcohol is represented as the second degree polynomial, Equation 51, for which the coefficients can be found in the appendix.

![Graph showing isentropic compressibility of primary alcohols as a function of temperature]

Figure 58: Isentropic Compressibility of primary alcohols as a Function of temperature

\[ \kappa_5(T) = AT^2 + BT + C \quad (51) \]

In addition to the four primary alcohols already discussed, 2-propanol and an azeotropic solution of hydrous ethanol were investigated to compare the effects of hydroxyl group location and purity. Initial density measurements revealed that both hydrous ethanol and 2-propanol exhibit properties that are vastly different from their pure and primary alcohol analogues. The presence of water in the 95% ethanol results in a dramatic increase in density, which is due to the effects it has on
molecular packing and attractive forces. Water’s high polarity and unique ability to form multiple hydrogen bonds results in stronger and more abundant intermolecular forces, which in turn creates larger and more densely packed clusters.

Conversely, by shifting the hydroxyl group from a terminal carbon to the secondary carbon, propanol becomes far less dense. By moving the electronegative oxygen to the center carbon propanol loses its linear shape and thus becomes less polar and also has a reduced capacity to support temporary dipoles. These changes substantially reduce dipole-dipole interactions and dispersion forces. Hydrogen bonding in 2-propanol is also reduced when compared to 1-propanol, as its non-linear shape inhibits close contact via steric effects. The reduced intermolecular forces and shape that is less conducive to close packing result in a reduced density. The structures of 1-propanol (A) and 2-propanol (B) are compared below in Figure 60.

![Figure 59: Density of alcohols as a function of temperature](image-url)
The hydrous sample of ethanol was observed to have a variable rate of change in velocity with respect to temperature. The curvature of the trend is subtle, but the quadratic coefficient is statistically non-zero at the 95% confidence level.

It is likely that the rate of change becomes slightly less negative over the temperature range as a result of the collapse of the hydrogen bonding network supported by water molecules. By reducing the number of hydrogen bonds the effects that the presence of water had on the density would be reduced significantly, effectively amplifying temperature’s effect on density. It is also plausible
that the increased disorder would compete with the typical temperature-related changes in compressibility in much the same way as it did in pure water, of course to a lesser extent.

In general, 2-propanol follows similar trends as the primary alcohols in that it decreases linearly as temperature is increased. However, velocity is significantly lower than that of 1-propanol. This is due to the large increase in compressibility, which is a result of the significantly reduced strength of intermolecular forces and packing efficiency. The reduced intermolecular attraction creates less rigid fluid and is therefore less conducive to rapid translation of compression waves.

![Figure 62: Isentropic compressibility of alcohols as a function of temperature](image)

Trends in isentropic compressibility are similar to those observed in primary alcohols, aside from the irregular magnitudes that coincide with observations made in velocity and density. However, by inspecting Figure 62 slight differences in the shape of the trends can be observed. There appears to be more curvature in the line corresponding to 95% ethanol, which supports the notion that as temperature increases there are changes to the mixture that have competing effects on
compressibility. In the case of 2-propanol, the overall change in compressibility is higher than those observed in the alcohols of similar size. This is because its comparably weaker intermolecular forces are more easily effected by increased kinetic energy.

Experimental and literature values of acoustic velocity, density, and isentropic compressibility at 25°C for each of the components are compared below in Table 9. In each instance the experimental values agree with those from literature, aside from the acoustic velocity measurement for 1-butanol. The difference in acoustic velocity is ~10.2 m/s, or about 0.815% of the literature value. This difference could be due to impurities introduced to the sample via cross contamination, a difference in sample purity, or simply due to temperature fluctuations. Regardless of the cause, the error is small enough that it can be considered negligible for the purposes of this project.

Table 9: Experimental and literature values for polar liquids at 25°C

<table>
<thead>
<tr>
<th>Entity</th>
<th>Acoustic Velocity (m/s)</th>
<th>Mass Density (kg/m3)</th>
<th>Compressibility (TPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Lit.</td>
<td>Exp.</td>
</tr>
<tr>
<td>Methanol</td>
<td>1114.9</td>
<td>1112ᵃ</td>
<td>789.31</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1154.9</td>
<td>1160ᵃ</td>
<td>787.68</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>1205.2</td>
<td>1208.1ᵇ</td>
<td>799.89</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1142.0</td>
<td>1141.3ᵇ</td>
<td>782.15</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>1251.0</td>
<td>1240.8ᵇ</td>
<td>806.96</td>
</tr>
<tr>
<td>Water</td>
<td>1500.4</td>
<td>1496.68³</td>
<td>996.93</td>
</tr>
</tbody>
</table>

[a] (Kumar et al., 1981)  [b] (Savaroglu & Aral, 2005)  [c] (Dougheret & Pal, 1990)

4.6.3 Measurements in binary mixtures of alcohols

In the final set of experiments, the effects of mixing on ultrasonic parameters were investigated. The mixtures under investigation include binary mixtures of methanol, 1-propanol, and 1-butanol in ethanol. Acoustic velocity, isentropic compressibility, and acoustic impedance were modeled as...
a function of volume percent of each liquid in ethanol. Experimental data for each parameter was fit with a least squares model and contrasted with ideal behaviour, which was calculated using the following equation:

$$v_{id} = \sqrt{\frac{V_{m}^{id}}{\kappa_{S}^{id} \rho_{m}^{id}}} = \frac{1}{\sqrt{\kappa_{S}^{id} \rho^{id}}}$$  \hspace{1cm} (52)$$

where superscript $id$ denotes the weighted average value based on mole fraction.

Figure 63: Acoustic velocity as a function of volume fraction

It was observed that within the investigated range (80-100% ethanol by volume) acoustic velocity varied linearly with volume fraction. Butanol was observed to have the most significant effect on acoustic velocity, followed by 1-propanol, and then methanol. Methanol was also the only alcohol that caused the acoustic velocity to decrease, this was expected as it is the only primary alcohol that exhibits slower speeds of sound than ethanol as a pure liquid.
In general, longer chained alcohols cause velocity to increase and shorter chained molecules cause it to decrease. However, the data does not coincide with ideal values calculated using Equation 52. This is because when the alcohols are mixed together they interact with one another via hydrogen bonding, dipole-dipole interactions, and dispersion forces, thus changing physical properties of the liquid. To better examine how the effects of mixing excess acoustic velocity was calculated as the difference between experimental and ideal values, and plotted as a function of volume fraction.

Figure 64: Excess acoustic velocity as a function of volume fraction

It was found that in all three cases the excess acoustic velocity was positive, and increased linearly with volume fraction. However, it is likely that if the experiment were extended to \( X = 1 \) a parabolic trend would emerge, with a maximum at about \( X = 0.5 \). The effects of mixing are the smallest in 1-propanol, this is because it displays properties most similar to those of ethanol. Because of their similar size, when propanol and ethanol are mixed together the new hydrogen bonds and dipole-dipole interactions that form will be very similar in strength to those in pure
ethanol. Methanol also has a similar carbon number as ethanol, but as it was discussed earlier, methanol’s singular carbon atom causes it to behave anomalously. Methanol’s slightly stronger polarity and hydrogen bonding potential is the likely cause of the positive excess velocity. In the case of 1-butanol and 1-propanol the excess can likely be attributed to the increased dispersion forces realized by their longer carbon chains.

The Stryjek-Vera modified Peng-Robinson equation of state was used to compute the density of each mixture. These values were then used to calculate isentropic compressibility via the Newton-Laplace equation and plotted as a function of volume fraction in ethanol.

![Figure 65: Compressibility as a function of volume fraction](image)

Ideal isentropic compressibilities were calculated as the-molar weighted average of the values for each of the pure alcohols in the mixture. After plotting compressibility as a function of volume fraction it was observed that within the parameters of this experiment the compressibility changed linearly with volume fraction in each scenario. Once again additions of butanol produced the most
significant changes, followed by propanol and then methanol. In the case of compressibility, methanol was the only alcohol that resulted in increasing compressibility in ethanol.

As was the case with acoustic velocity, the experimental sets of data do not agree with the ideal models. However, in this case the excess quantities were negative in each instance, implying that intermolecular forces between molecules of the alcohol being added and ethanol are stronger than those between two ethanol molecules. The rationale behind this is that the ideal condition assumes that intermolecular forces are added linearly, for example it assumes that the strength of methanol-ethanol forces are the average of methanol-methanol and ethanol-ethanol forces. This can be attributed to larger dispersion forces in propanol and butanol, and increased polarity and hydrogen bonding potential in methanol.

![Excess compressibility as a function of volume fraction](image)

**Figure 66: Excess compressibility as a function of volume fraction**

The Stryjek-Vera modified Peng-Robinson density values were very similar to the ideal values calculated using mole fractions, so trends in acoustic impedance are nearly identical to those in
acoustic velocity and provide very little insight or information regarding the effects of mixing on the physical properties of the alcohols. However, the sign of the excess density values does deviate from the patterns observed thus far and provide evidence of methanol’s anomalous behaviour.

![Figure 67: Excess density as a function of volume fraction](image)

Methanol’s unique density properties were discussed in a previous section, wherein its irregularly high density was attributed to its propensity to form closely packed clusters supported by hydrogen bonds. When mixed with ethanol, methanol causes a net increase in density. The ideal model predicts this, as methanol is slightly denser than ethanol. However, the realized rate of change in density is actually lower than the one predicted by the ideal equation. Whereas in propanol and butanol it is greater. This is because the effects of methanol’s unique hydrogen bonding capability are diminished when interacting with ethanol, compared to another molecule of methanol.
4.6.4 Practical applications

3.6.4.1 Estimation of water content in ethanol

The previous section demonstrated the ability of ultrasonic techniques to detect changes in concentration, even under conditions where mixtures are composed of very similar liquids. A potential application for these techniques is detecting the presence of water in an ethanol sample. To investigate the viability of ultrasonic monitoring for these purposes, water was added to ethanol over a range of 0-20% by volume, with the temperature held at 30°C. One-thousand time-of-flight readings were collected over the span of 10 seconds at various points throughout the range and subsequently used to compute acoustic velocity. The resulting data was plotted as a function of volume fraction.

![Acoustic velocity as a function of water content in ethanol](image)

Figure 68: Acoustic velocity as a function of water content in ethanol

\[ v(X) = -1136.4X^2 + 1052.4X + 1143.9 \] (53)

Acoustic velocity was found to vary according to a second degree polynomial, which can be seen in Equation 53. In addition to fitting a least squares model, 95% confidence bands were calculated.
and are shown in Figure 68. Though the confidence interval varies, due to the non-linear spacing of the data points, the average half-width of the confidence interval is 0.783 vol%. Therefore, given a value of acoustic velocity, the water content of an ethanol sample can be determined within ±0.783% by volume, with 95% confidence. Additional testing would increase degrees of freedom, thereby reducing the standard error and providing a more accurate model.

The Stryjek-Vera modified Peng-Robinson equation of state was used to calculate density data, which was then used to compute compressibility over the same range that velocity was investigated.

![Graph showing isentropic compressibility as a function of water content in ethanol](image)

**Figure 69: Isentropic compressibility as a function of water content in ethanol**

\[ \kappa_5(X) = 2858.9X^2 - 1719.3X + 974.82 \]  

(54)

Compressibility was also fit using a second order polynomial with 95% confidence bands. Compressibility was observed to decrease with a rate of change that became less negative as water content increased. This trend is favorable for the purposes of monitoring ethanol-water mixtures as they approach the azeotrope, because the increased rate of change in the ethanol-rich region can
provide greater accuracy. The uncertainty using compressibility is slightly higher than in it was with the velocity example; being accurate within ±0.978% by volume at the 95% confidence level. However, this model is based on only 7 data points, so with only 6 degrees of freedom the standard error is quite high. The width of the confidence intervals could be greatly reduced if sampling frequency is increased, yielding a more precise prediction model.

Next the effects of water content on acoustic impedance were investigated. Acoustic impedance, like compressibility, accounts for density as well as acoustic velocity, and since both quantities increase as water is added to ethanol it is reasonable to expect that impedance will provide a better model for prediction.

\[ Z(X) = -889.01X^2 + 829.41X + 896.46 \] (55)

Again, the data was fit with a second order polynomial with 95% confidence bands. As expected, acoustic impedance increases as water content increases. However, there was no significant increase in accuracy of the model, only decreasing the uncertainty to ±0.776% by volume.
Although this is most precise of the 3 correlations discussed, there would undoubtedly be significant added costs and complexity associated with taking both density and time-of-flight measurements. In order to assess whether or not the increased precision is worth the additional investment a more in-depth analysis of the precision limits must be performed. The decision would also be specific to the application for which it is intended to be used.

Figure 71: Schematic of potential ultrasonic ethanol hydration monitoring system

3.6.4.2 Estimation of ethanol content in gasoline

Another potential practical application for monitoring of binary mixtures via ultrasonic technology is estimating ethanol content in gasoline. However, it should be pointed out that gasoline is itself a complex mixture, so the ethanol-gasoline mixture is not truly binary. However, it was demonstrated in chapter 3 that complex mixtures can be treated as a single liquid when tracking changes in concentration of a targeted component. In the following experiments ethanol was systematically added to n-heptane (which was used to model gasoline), and tested at various concentrations between 0 and 30% by volume.

Upon initial additions of ethanol, a significant drop in acoustic velocity was realized. This observation agrees with results from previous sections that suggest that smaller molecules are less
conducive to rapid propagation of ultrasound. However, in the case of ethanol this is somewhat peculiar, as pure ethanol exhibits slightly higher speeds of sound than pure n-heptane; 1146 m/s (D'Arrigo & Paparelli, 1988) and 1113 m/s (Oswal & Maisura, 2002), respectively.

The variation in behaviour is due to the differences between the structures of heptane and ethanol. Ethanol is polar, whereas heptane is not. Ethanol’s polarity and the presence of an O-H bond facilitate dipole-dipole interactions and hydrogen bonding, when in a pure state or mixed with a similar liquid. However, when in low concentrations in a non-polar liquid ethanol molecules have a very low probability of interacting with other polar molecules. Thus ethanol is unable to participate in the interactions that cause its high acoustic velocity.

![Acoustic velocity as a function of ethanol content in n-heptane](image)

Figure 72: Acoustic velocity as a function of ethanol content in n-heptane

\[ v(X) = \frac{1092X + 73.94}{X + 0.06645} \]  (56)

The effects of mixing ethanol and an alkane differ from those observed in binary mixtures of alcohols in that the rate of change in acoustic velocity becomes less negative as ethanol content increases. The decreasing rate of change and similar pure-component acoustic velocities suggest that if the experiment were continued beyond 30 vol%, velocity may begin to increase with each
addition, resulting in a parabolic-like trend. This suggests that in low concentrations the effects of ethanol’s polarity are not strong enough to overcome the effects of its reduced size. Since dipole-dipole interactions and hydrogen bonding occur between neighboring polar molecules at low concentrations the probability of two polar molecules being adjacent is lower. So as the concentration of ethanol increases, more ethanol molecules have the opportunity to participate in dipole-dipole interactions and hydrogen bonding. Thus, increasing the overall strength of intermolecular forces and ultimately, having a positive impact on acoustic velocity.

The initial high rate of change in velocity is attractive for determining the concentration at low ethanol content, between about 0-10% by volume. Beyond this the low rate of change becomes problematic, as even narrow confidence intervals provide a large uncertainty for ethanol content estimations.

Figure 73: Isentropic compressibility as a function of ethanol content in n-heptane

The Stryjek-Vera modified Peng-Robinson equation of state was used to calculate the density of each mixture, which was then used to compute isentropic compressibility. Again, the response to
additions of ethanol was vastly different from those observed from alkane additions. In the case of ethanol, compressibility increased with a decaying rate of change before reaching a maximum value at ~10 vol%. Beyond which point compressibility decreased with ethanol content and the rate of change continued to become more negative. This trend supports the logic used to explain how velocity varied with ethanol concentration, as compressibility is inversely proportional to the strength of intermolecular forces. This curve is interesting, and provides validation and insight of previous theories. However, on its own is not useful for determining ethanol content in gasoline over the entire range, as most values of compressibility correspond to 2 different values of X (ethanol content).

Figure 74: Acoustic impedance as a function of ethanol content in n-heptane

Acoustic impedance also exhibits a parabolic shape. Initially decreasing as water is added, before reaching a minimum and increasing dramatically. Although the data for impedance fits a rational function quite well, it is not useful for deducing ethanol content over the entire domain because impedance values at the lower end of the range correspond to multiple volume fractions.
To circumvent the issues that arise from the system’s tendency to behave parabolically, the data must be fit with piecewise functions. Since multiple functions will be used to fit different sections of the data it is logical to use each of the three correlations discussed above to maximize precision. For example, the rate of change in isentropic compressibility is large when \( X < 0.06 \), compared to acoustic impedance which is most drastically effected when \( X \) is greater than 0.1. Since greater rates of change yield higher precision, each of these parameters will be used within these respective ranges.

Figure 75: Piecewise functions for estimating ethanol content in n-heptane

An initial estimation of ethanol content will be made using Equation 56, from this it will be determined which piecewise function is appropriate for determining ethanol content to a higher precision. Table 10 summarizes each of the three piecewise functions, including their intended range, the function itself, and mean uncertainty.
Table 10: Summary of correlations for determining ethanol content in n-heptane

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range (vol/vol)</th>
<th>Equation</th>
<th>Uncertainty (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isentropic compressibility</td>
<td>0.00-0.45</td>
<td>$X = 0.08243 - 0.01992\sqrt{1213.72 - \kappa_s}$</td>
<td>± 0.00369</td>
</tr>
<tr>
<td>Acoustic velocity</td>
<td>0.46-0.10</td>
<td>$X = \frac{v - 1108.3}{-81.042}$</td>
<td>± 0.00528</td>
</tr>
<tr>
<td>Acoustic impedance</td>
<td>&gt;0.10</td>
<td>$X = \sqrt{\frac{Z - 746.91}{212.44}}$</td>
<td>± 0.00026</td>
</tr>
</tbody>
</table>

Using amplitude values at each measurement, and the amplitude of a reference measurement in pure heptane, attenuation coefficient was calculated over the entire concentration range.

![Figure 76: Attenuation coefficient as a function of ethanol content in n-heptane](image)

Figure 76: Attenuation coefficient as a function of ethanol content in n-heptane

\[ \alpha = \frac{1}{d} \ln \left[ \frac{A_{\text{ref}}}{A_{\text{unknown}}} \right] = \frac{X(10.89 - 1.262X)}{X^2 + 9.171} \]  

(57)

Between 0 and 2% ethanol attenuation coefficient increased as a function of ethanol, with a decaying rate of change. However, beyond the maximum at 2%, additions of ethanol caused attenuation coefficient to decrease and with each addition the rate of change became less negative. This behaviour is somewhat consistent with that of velocity and compressibility; initially the
effects of ethanol additions resemble those of the additions of small alkanes, but as ethanol concentration increases the effects become more like those of a longer chain alkane. Again, this is thought to be due to the increased probability of polar molecules interacting.

Attenuation coefficient can be used as a check to validate the ethanol content calculated using the correlations dependent upon TOF and density.

Figure 77: Schematic of potential ethanol content monitoring system for gasoline

Figure 78: Proposed ethanol content monitoring algorithm
4.7 Conclusions

Measurements of ultrasonic parameters in this chapter demonstrated the distinct difference between polar and non-polar molecules. This is especially true of water, which has anomalous behaviour that is incomparable to that of any other liquid investigated. The unique behaviour exhibited by water stems from unique hydrogen bonding properties, and propensity to form highly ordered molecular clusters. In water heating results in a drop in compressibility, and ultimately increases ultrasonic velocity and impedance. Conversely, alcohols exhibit increased compressibility when heated, due to increased spacing between molecules, resulting in lower acoustic velocity and impedance.

In addition to temperature effects, the primary alcohols ultrasonic parameters displayed a dependence upon molecular size. Acoustic velocity and impedance were both higher in larger molecules, while compressibility was lower. This was attributed to the increased dispersion forces present in molecules with longer chain lengths. However, when 2-propanol was compared to the primary alcohols it was observed to behave as a much smaller molecule; having properties between those of ethanol and methanol. This observation showcases the effects of reduced polarity on packing efficiency and intermolecular forces.

Experiments in binary mixtures of water, methanol, 1-propanol, and 1-butanol in ethanol produced results that deviated from ideal behaviour dramatically, with excess quantities increasing with the degree of mixing. Despite their non-ideal behaviour, changes in each parameter had quantifiable trends, which could potentially be used for deducing the concentration of a binary mixture.

In the case of water-ethanol mixtures acoustic velocity, acoustic impedance, and isentropic compressibility all varied according to second order polynomials with respect to the volume fraction of water. When used to predict water content in ethanol between 0 and 20% by volume,
the uncertainty for the 3 functions were ±0.783, ±0.776, and ±0.973 vol%, respectively. Although acoustic impedance produced the most precise model, the velocity based does not require density data which simplifies the equipment and computations.

The final set of tests examined the effects of adding ethanol to n-heptane, which was used to simulate gasoline. The resulting curves displayed regions of irregular behaviour that made them unsuitable for deducing ethanol concentration over the entire range of 0-30%. To resolve this issue, the curves were fit with piecewise functions in areas where rate of change was highest to maximize precision. An algorithm was developed to determine which piecewise function was appropriate for a given sample and to subsequently report an estimate. The algorithm also included attenuation coefficient comparisons with a reference liquid to confirm the validity of the estimation.

4.8 Recommendations

The ultrasonic probe used in this experimental study featured an epoxy coating to protect the ultrasonic probe’s internal components from liquid damage. Unfortunately, the coating slowly deteriorated over time in alcohol solutions, so the probe had to be removed and inspected and cleaned to maintain its integrity. Frequent removal and submerging the probe caused temperature fluctuations and likely affected the concentrations of the binary mixtures. Accurate amplitude readings were also unattainable, as the measurements can take up to several minutes to stabilize and the probe could only be exposed for ~30 seconds at a time. To resolve this issue a more versatile protective coating should be implemented in the future, possible materials may include Teflon or a ceramic. A more durable probe would also allow for more experiments to be done, yielding more data and thereby better correlations. This could significantly reduce the confidence intervals as increasing degrees of freedom would reduce the standard error.
In the ethanol-heptane mixtures, heptane should be replaced with commercial gasoline to show that the concept can be adapted to real-world situations. The effects of methanol additions could be investigated as well, as it is commonly added to gasoline as a stabilizing agent.

In future experiments the effects of salinity could be expanded upon to include a variety of mineral salts; including chlorides of magnesium and calcium. This and an increased temperature range would help to liken experimental conditions to those of industry.
4.9 References


Chapter 5: Overall conclusions and recommendations

Conventional techniques for liquid-phase process monitoring exhibit adverse attributes making them unfavourable for many on-line applications. Ultrasonic monitoring shows promise as an alternative technique, being robust, compact, adaptable and inexpensive.

Within the parameters of the experiments conducted for this report, it has been demonstrated that ultrasonic technology is a viable option of on-line liquid characterization in pure liquids and their mixtures. Ultrasonic velocity, acoustic impedance, and isentropic compressibility show strong correlations with the variables under investigation. Said correlations have been used in the following proposed applications:

- estimation of carbon number in paraffinic liquids
- detection of impurities in a liquid sample
- monitoring volatile losses from complex mixtures
- estimating water concentration in ethanol
- estimating ethanol content in gasoline

Proof of concept was provided for the detection of impure samples, as discussed in chapter 3. Preliminary drafts of algorithms for determining ethanol content in gasoline and carbon number of paraffinic liquids are proposed and can be found in Chapter 4 and Appendix C, respectively.

It is recommended that future research considers the effects of frequency on different ultrasonic parameters. Different materials for the probe’s protective coating should be tested in an attempt to obtain more consistent amplitude readings, allowing for a more in-depth analysis of attenuation. The way attenuation coefficient is analyzed should also be re-evaluated; by employing a probe with multiple receivers with different associated path lengths one can solve for absolute attenuation, instead of relating data to an arbitrary reference liquid.
Chapter 6: Appendices

6.1 Appendix A: Tables of coefficients for chapter 3

Table 11: Coefficients for velocity on n-alkanes as a function of carbon number

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>280.57</td>
<td>583.45</td>
<td>0.99314</td>
</tr>
<tr>
<td>30</td>
<td>285.97</td>
<td>550.90</td>
<td>0.99312</td>
</tr>
<tr>
<td>40</td>
<td>295.65</td>
<td>488.24</td>
<td>0.99228</td>
</tr>
<tr>
<td>50</td>
<td>306.63</td>
<td>423.52</td>
<td>0.99188</td>
</tr>
<tr>
<td>60</td>
<td>315.34</td>
<td>364.45</td>
<td>0.99223</td>
</tr>
</tbody>
</table>

Table 12: Coefficients for compressibility of n-alkanes as a function of carbon number

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4173.9</td>
<td>-0.65910</td>
<td>0.98641</td>
</tr>
<tr>
<td>30</td>
<td>4551.3</td>
<td>-0.67968</td>
<td>0.98902</td>
</tr>
<tr>
<td>40</td>
<td>5450.0</td>
<td>-0.72301</td>
<td>0.98767</td>
</tr>
<tr>
<td>50</td>
<td>6609.2</td>
<td>-0.77144</td>
<td>0.98667</td>
</tr>
<tr>
<td>60</td>
<td>8002.2</td>
<td>-0.81836</td>
<td>0.98641</td>
</tr>
</tbody>
</table>

Table 13: Coefficients for velocity as a function of temperature

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>-4.5177</td>
<td>1191.5</td>
<td>0.99983</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>-4.3208</td>
<td>1242.7</td>
<td>0.99994</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>-4.0138</td>
<td>1306.5</td>
<td>0.99996</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>-3.8301</td>
<td>1371.0</td>
<td>0.99989</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>-4.7998</td>
<td>1370.9</td>
<td>0.99986</td>
</tr>
<tr>
<td>isoHexane</td>
<td>-4.5143</td>
<td>1167.2</td>
<td>0.99975</td>
</tr>
<tr>
<td>isoOctane</td>
<td>-4.1292</td>
<td>1184.7</td>
<td>0.99988</td>
</tr>
<tr>
<td>Toluene</td>
<td>-4.3732</td>
<td>1413.7</td>
<td>0.99919</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>-3.5345</td>
<td>1513.3</td>
<td>0.99985</td>
</tr>
</tbody>
</table>
Table 14: Coefficients for density as a function of temperature

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>-1.0683</td>
<td>684.24</td>
<td>0.99909</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>-0.9179</td>
<td>702.93</td>
<td>0.99563</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>-0.9192</td>
<td>738.89</td>
<td>0.99806</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>-0.8174</td>
<td>765.91</td>
<td>0.99964</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>-1.0349</td>
<td>800.86</td>
<td>0.99660</td>
</tr>
<tr>
<td>isoHexane</td>
<td>-1.0326</td>
<td>680.03</td>
<td>0.99683</td>
</tr>
<tr>
<td>isoOctane</td>
<td>-0.9520</td>
<td>713.03</td>
<td>0.99482</td>
</tr>
<tr>
<td>Toluene</td>
<td>-1.0047</td>
<td>887.05</td>
<td>0.99999</td>
</tr>
</tbody>
</table>

Table 15: Coefficients for isentropic compressibility as a function of temperature

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>0.12559</td>
<td>6.2938</td>
<td>1072.5</td>
<td>0.99997</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.08559</td>
<td>5.6515</td>
<td>948.08</td>
<td>0.99998</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.05407</td>
<td>4.7475</td>
<td>807.99</td>
<td>0.99999</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>0.03626</td>
<td>3.9419</td>
<td>703.87</td>
<td>0.99999</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>0.06258</td>
<td>4.0721</td>
<td>684.17</td>
<td>0.99998</td>
</tr>
<tr>
<td>isoHexane</td>
<td>0.13018</td>
<td>7.0489</td>
<td>1118.1</td>
<td>0.99998</td>
</tr>
<tr>
<td>isoOctane</td>
<td>0.09406</td>
<td>6.1418</td>
<td>1028.9</td>
<td>0.99998</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.02583</td>
<td>4.2155</td>
<td>559.80</td>
<td>0.99980</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>0.03660</td>
<td>3.3162</td>
<td>502.78</td>
<td>0.99989</td>
</tr>
</tbody>
</table>

Table 16: Coefficients for compressibility power-coefficients as a function of temperature

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>γ</th>
<th>δ</th>
<th>ε</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.20653</td>
<td>6.7014</td>
<td>3256.5</td>
<td>0.99998</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>-4.5692x10⁻³</td>
<td>-0.54298</td>
<td>0.99926</td>
</tr>
</tbody>
</table>
Table 17: Coefficients for acoustic velocity as a function of volume fraction in n-heptane

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>0</td>
<td>-54.892</td>
<td>1113.0</td>
<td>0.99831</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>32.988</td>
<td>80.738</td>
<td>1112.7</td>
<td>0.99908</td>
</tr>
<tr>
<td>isoHexane</td>
<td>-7.7740</td>
<td>-73.020</td>
<td>1113.4</td>
<td>0.99902</td>
</tr>
<tr>
<td>isoOctane</td>
<td>0</td>
<td>-50.283</td>
<td>1112.4</td>
<td>0.99703</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0</td>
<td>73.928</td>
<td>1110.3</td>
<td>0.99764</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>0</td>
<td>150.53</td>
<td>1108.9</td>
<td>0.99764</td>
</tr>
</tbody>
</table>

Table 18: Coefficients for compressibility as a function of volume fraction in n-heptane

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>23.031</td>
<td>156.93</td>
<td>1195.2</td>
<td>0.99972</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>23.031</td>
<td>-355.46</td>
<td>1196.1</td>
<td>0.99968</td>
</tr>
<tr>
<td>isoHexane</td>
<td>50.734</td>
<td>199.19</td>
<td>1194.6</td>
<td>0.99943</td>
</tr>
<tr>
<td>isoOctane</td>
<td>13.870</td>
<td>84.698</td>
<td>1197.1</td>
<td>0.99550</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>11.223</td>
<td>-209.32</td>
<td>1198.4</td>
<td>0.99907</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>64.826</td>
<td>-416.36</td>
<td>1199.3</td>
<td>0.99906</td>
</tr>
</tbody>
</table>

Table 19: Coefficients for attenuation in n-alkanes as a function of temperature

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptane</td>
<td>-0.00176</td>
<td>0.07753</td>
<td>-1.39642</td>
<td>0.99777</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>-0.00125</td>
<td>0.05645</td>
<td>0.05645</td>
<td>0.99753</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>-0.00185</td>
<td>0.08098</td>
<td>0.08098</td>
<td>0.99781</td>
</tr>
</tbody>
</table>

Table 20: Coefficients for attenuation in other hydrocarbons as a function of temperature

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>cycloHexane</td>
<td>-0.02507</td>
<td>-8.6255</td>
<td>0.93741</td>
</tr>
<tr>
<td>isoHexane</td>
<td>0.01284</td>
<td>2.5446</td>
<td>0.96542</td>
</tr>
<tr>
<td>isoOctane</td>
<td>-0.06725</td>
<td>0.02373</td>
<td>0.94272</td>
</tr>
</tbody>
</table>
6.2 Appendix B: Tables of coefficients for chapter 4

Table 21: Coefficients for velocity as a function of temperature in water

<table>
<thead>
<tr>
<th>Liquid</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>-0.02312</td>
<td>3.2478</td>
<td>1435.4</td>
<td>0.97971</td>
</tr>
<tr>
<td>DI Water</td>
<td>-0.03262</td>
<td>3.9647</td>
<td>1421.7</td>
<td>0.99774</td>
</tr>
</tbody>
</table>

Table 22: Coefficients for compressibility as a function of temperature in water

<table>
<thead>
<tr>
<th>Liquid</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>0.01505</td>
<td>-1.8210</td>
<td>480.23</td>
<td>0.96616</td>
</tr>
<tr>
<td>DI Water</td>
<td>0.02105</td>
<td>-2.2744</td>
<td>489.27</td>
<td>0.99690</td>
</tr>
</tbody>
</table>

Table 23: Coefficients for impedance as a function of temperature in water

<table>
<thead>
<tr>
<th>Liquid</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>-0.02807</td>
<td>3.0046</td>
<td>1441.3</td>
<td>0.93194</td>
</tr>
<tr>
<td>DI Water</td>
<td>-0.03951</td>
<td>3.8548</td>
<td>1424.1</td>
<td>0.99316</td>
</tr>
</tbody>
</table>

Table 24: Linear salinity coefficients

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>A</th>
<th>A_{LCL}</th>
<th>A_{UCL}</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Acoustic Velocity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>10.588</td>
<td>10.195</td>
<td>10.980</td>
<td>1511.5</td>
<td>0.99589</td>
</tr>
<tr>
<td>60</td>
<td>8.9405</td>
<td>8.4548</td>
<td>9.4261</td>
<td>1542.1</td>
<td>0.99122</td>
</tr>
<tr>
<td><strong>Isentropic Compressibility</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-9.1821</td>
<td>-9.4244</td>
<td>-8.9397</td>
<td>439.68</td>
<td>0.99792</td>
</tr>
<tr>
<td>60</td>
<td>-7.9565</td>
<td>-8.2336</td>
<td>-7.6794</td>
<td>428.49</td>
<td>0.99637</td>
</tr>
<tr>
<td><strong>Acoustic Impedance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>21.932</td>
<td>21.545</td>
<td>22.318</td>
<td>1504.5</td>
<td>0.99907</td>
</tr>
<tr>
<td>60</td>
<td>20.163</td>
<td>19.685</td>
<td>20.640</td>
<td>1513.1</td>
<td>0.99832</td>
</tr>
</tbody>
</table>
Table 25: Coefficients for velocity in primary alcohols as a function of carbon number

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>45.852</td>
<td>1066.9</td>
<td>0.99728</td>
</tr>
<tr>
<td>30</td>
<td>45.440</td>
<td>1051.5</td>
<td>0.99809</td>
</tr>
<tr>
<td>40</td>
<td>44.617</td>
<td>1020.6</td>
<td>0.99930</td>
</tr>
<tr>
<td>50</td>
<td>43.793</td>
<td>989.76</td>
<td>0.99993</td>
</tr>
<tr>
<td>60</td>
<td>42.970</td>
<td>958.91</td>
<td>0.99990</td>
</tr>
</tbody>
</table>

Table 26: Coefficients for velocity in alcohols as a function of temperature

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>-3.2403</td>
<td>1195.9</td>
<td>0.99507</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-3.1265</td>
<td>1233.1</td>
<td>0.99773</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>-3.3582</td>
<td>1289.2</td>
<td>0.99883</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>-3.4375</td>
<td>1336.9</td>
<td>0.99623</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>-3.4270</td>
<td>1227.7</td>
<td>0.99950</td>
</tr>
<tr>
<td>95% Ethanol</td>
<td>-3.3477</td>
<td>1293.6</td>
<td>0.99280</td>
</tr>
</tbody>
</table>

Table 27: Coefficients for density of alcohols a function of temperature

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>-0.00593</td>
<td>-0.47038</td>
<td>803.15</td>
<td>0.99720</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-0.00505</td>
<td>-0.54074</td>
<td>816.56</td>
<td>0.99862</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>-0.00675</td>
<td>-0.44694</td>
<td>823.26</td>
<td>0.99976</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>-0.00437</td>
<td>-0.07823</td>
<td>1001.6</td>
<td>0.99983</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>-0.00797</td>
<td>-0.34671</td>
<td>795.8</td>
<td>0.99879</td>
</tr>
<tr>
<td>95% Ethanol</td>
<td>-0.00588</td>
<td>-0.39628</td>
<td>820.54</td>
<td>0.99806</td>
</tr>
</tbody>
</table>
Table 28: Coefficients for compressibility of alcohols as a function of temperature

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.04556</td>
<td>4.5526</td>
<td>877.26</td>
<td>0.99834</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.03342</td>
<td>4.2822</td>
<td>824.43</td>
<td>0.99909</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.02786</td>
<td>4.4591</td>
<td>730.28</td>
<td>0.99834</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.03550</td>
<td>2.9656</td>
<td>696.50</td>
<td>0.99977</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.04831</td>
<td>4.4174</td>
<td>840.50</td>
<td>0.99932</td>
</tr>
<tr>
<td>95% Ethanol</td>
<td>0.04782</td>
<td>2.6978</td>
<td>749.46</td>
<td>0.99990</td>
</tr>
</tbody>
</table>

Table 29: Coefficients for acoustic velocity as a function of volume fraction in ethanol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>-35.531</td>
<td>1139.3</td>
<td>0.99823</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>47.262</td>
<td>1139.3</td>
<td>0.99974</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>91.009</td>
<td>1139.3</td>
<td>0.99958</td>
</tr>
</tbody>
</table>

Table 30: Coefficients for excess velocity as a function of volume fraction in ethanol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>20.482</td>
<td>0.13013</td>
<td>0.98880</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>9.9609</td>
<td>0.03649</td>
<td>0.99612</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>34.140</td>
<td>0.13212</td>
<td>0.99216</td>
</tr>
</tbody>
</table>

Table 31: Coefficients for compressibility as a function of volume fraction in ethanol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>60.56842</td>
<td>983.0089</td>
<td>0.99816</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>-95.46825</td>
<td>983.02193</td>
<td>0.99986</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>-177.28217</td>
<td>982.90295</td>
<td>0.99947</td>
</tr>
</tbody>
</table>
Table 32: Coefficients for excess compressibility as a function of volume fraction in ethanol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>-35.760</td>
<td>-0.20565</td>
<td>0.98998</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>-19.551</td>
<td>-0.08350</td>
<td>0.99639</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>-64.022</td>
<td>-0.30524</td>
<td>0.99085</td>
</tr>
</tbody>
</table>
6.3 Appendix C: Potential practical applications for chapter 3

6.3.1 Monitoring concentration

The significant differences in ultrasonic parameters observed in similar organic liquids showcase its potential for monitoring the concentration of a mixture with known components, or to detect the presence of an unknown component. Applications for this type of technology include monitoring the extent of which a reaction has gone to completion by tracking the concentration of reactants or products, monitoring the efficacy of a distillation tower or other purification unit, or simply as a preliminary quality check for intermediate or final products.

![Figure 79: Schematic of potential ultrasonic concentration monitoring system](image)

The proposed set up would include a probe (possibly multiple) inserted into the pipeline, reservoir, vessel or reactor under observation. The probe would be equipped to take time of flight, amplitude, and temperature readings and would send the information to a pulser/receiver unit capable of relaying the data to a computer. A second identical probe would be inserted into a small bench-top tank with a reference liquid (likely the desired product) at a controlled temperature and pressure. Time of flight values will then be used to calculate acoustic velocity for both sets of data for comparison, and attenuation of the sample under observation will be calculated using the control’s
amplitude data as reference peaks. Comparing the unknown sample to reference using an identical probe will reduce error by creating a paired test. In order for this to be effective probes must be inspected frequently and tested in a common environment to ensure that they have identical functionality. For more complex systems, or to create redundancy checks, the probe could be modified to take density measurements of the liquid as well. By doing this the compressibility, acoustic impedance could also be tracked.

6.3.2 Monitoring losses in crude oil

The proposed system for monitoring crude oil losses is similar to the system proposed for determining product purity, because essentially, they do the same thing. However, with crude oil storage the probes will need to be dispersed throughout the tank in order to account for separation. Another key distinction is that the amplitude monitoring should be equipped to detect precipitation of solids, such as asphaltenes, by employing ultrasonic particle sizing techniques similar to those suggested by Shukla et al. (2010). By estimating the amount of heavy fractions precipitating out of solution, one can theoretically account its effects on acoustic velocity.

![Schematic of proposed ultrasonic crude oil losses monitoring system](image)

Figure 80: Schematic of proposed ultrasonic crude oil losses monitoring system
6.3.3 Estimating carbon number

In a chapter 3 it was demonstrated that carbon number could be estimated using ultrasonic parameters, given that the liquid is a normal alkane. The problem with said application is that in practice there are very few situations where one is certain of an unknown liquids molecular shape, but not its length. To rectify this issue, an algorithm was developed to check whether carbon number estimates obtained using n-alkane trends are accurate.

![Figure 81: Schematic of proposed ultrasonic carbon number estimation system](image)

The proposed system would require measurements of density, temperature, and time of flight. Using these measured values acoustic velocity, acoustic impedance, and isentropic compressibility can be computed. The three calculated values along with the density measurement will then be used to generate four individual estimates of carbon number using empirical correlations for n-alkanes.
Figure 82: Carbon number estimation plots for algorithm

If the values are not reasonably similar this is an indication that the sample contains high levels of non-ideal components and the carbon number estimations are inaccurate. If each value is reasonably close, the carbon number estimated via acoustic velocity will be used to generate apparent values of density, compressibility, and impedance using the same empirical correlations.
The next check for accuracy is done by comparing the apparent parameters to their corresponding experimental values. This can be done using a plot of apparent vs experimental values such as the ones shown in Figure 83. The line for comparison was generated using n-alkane data, and the confidence bands are representative of a 95% confidence interval. The above test was able to generate accurate carbon number estimations for all n-alkanes, isohexane, and mineral oil. It was also able to determine that cyclohexane, toluene, and iso-octane did not fit the model. This can be seen in Figure 83 as they are the only points that lie outside the confidence interval.

Table 33: Evaluation of carbon number estimation algorithm

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Calculated C</th>
<th>Absolute Error</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>5.8652</td>
<td>0.13481</td>
<td>2.25%</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>7.1006</td>
<td>0.10058</td>
<td>1.44%</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>9.2567</td>
<td>0.25668</td>
<td>2.85%</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>11.767</td>
<td>0.23291</td>
<td>1.94%</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>23.401</td>
<td>2.4008</td>
<td>11.43%</td>
</tr>
<tr>
<td>isoHexane</td>
<td>5.5370</td>
<td>0.46300</td>
<td>7.72%</td>
</tr>
</tbody>
</table>
The error is higher in the mineral oil and isohexane, which is to be expected as the algorithm is tuned to determine carbon number of n-alkanes. The reason that isohexane was not omitted via the algorithm is likely because it only has a single branched methyl group, whereas iso-octane has 3. Therefore, isohexane has properties that more closely resemble those of a normal alkane. An overview of the complete proposed algorithm can be seen below.

![Proposed carbon number determination algorithm](image)

Figure 84: Proposed carbon number determination algorithm

Both toluene and cyclohexane were eliminated at the initial check, where carbon number estimates were compared. The difference between maximum and minimum estimates for cyclohexane was about 4, while in toluene the range was approximately 16. This test was unable to identify iso-octane as a non-normal alkane, as its estimations only had a range of 1.6 (about 10% of that in toluene). However, the second set of checks was able to distinguish iso-octane as non-normal, causing the algorithm to reject its estimated carbon number of approximately 6.
Chapter 7: Curriculum Vitae

Name: William Alec Cooke

Post-secondary Education and Degrees:
The University of Western Ontario
London, Ontario, Canada
MESc: Chemical Engineering – 2016 (in progress)
The University of Western Ontario
London, Ontario, Canada
BSc: Chemistry – 2016
The University of Western Ontario
London, Ontario, Canada
BESc: Chemical and Engineering – 2015

Honours and Awards:
1st Place at Research Bridges Symposium: Chemical Engineering – 2016
Western Research Graduate Scholarship – 2015, 2016
Dean’s Honour List – 2014, 2015, 2016
125th Anniversary Alumni Award in Engineering – 2014
Queen Elizabeth II Aiming for the Top Scholarship – 2009
The Western Scholarship of Distinction – 2009

Related Work Experience:
Graduate Research Assistant
The University of Western Ontario
Department of Chemical and Biochemical Engineering
May 2015 – August 2016
Teaching Assistant: Engineering Communications
The University of Western Ontario
Sept. 2015 – April 2016
Undergraduate Research Assistant
The University of Western Ontario
Department of Chemical and Biochemical Engineering
May 2014 – August 2014

Past Academic Projects:
A Unique Approach to Naphtha Desulfurization – 2015
Measurements of Ultrasonic Wave Parameters for On-Line Characterization of Liquids – 2015